

PB-237 374

PRECIPITATION SCAVENGING OF INORGANIC
POLLUTANTS FROM METROPOLITAN SOURCES

M. T. Dana, et al

Battelle-Pacific Northwest Laboratories

Prepared for:

National Environmental Research Center

June 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

PRECIPITATION SCAVENGING OF INORGANIC POLLUTANTS FROM METROPOLITAN SOURCES

by

M.T. Dana, J.M. Hales,
C.E. Hane, and J.M. Thorp

Atmospheric Sciences Dept., Battelle,
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington 99352

Interagency Agreement No. IAG-D4-0323
Program Element No. 1AA009

EPA Project Officer: Herbert Viebrock

Meteorology Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared for
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

June 1974

ia

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1. REPORT NO. EPA-650/3-74-005		3. RE PB 237 374
4. TITLE AND SUBTITLE Precipitation Scavenging of Inorganic Pollutants from Metropolitan Sources		5. REPORT DATE
7. AUTHOR(S) M..T. Dana, J. M. Hales, C. E. Hane, and J. M. Thorp		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Sciences Dept. Battelle-Pacific Northwest Laboratories P. O. Box 999 Richland, Washington 99352		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Meteorology Laboratory National Environmental Research Center Environmental Protection Agency Research Triangle Park, N. C. 27711		10. PROGRAM ELEMENT NO. 1AA009
		11. CONTRACT/GRANT NO. IAG-D4-0323
		13. TYPE OF REPORT AND PERIOD COVERED Final: July '72-June '74
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		
16. ABSTRACT This report describes initial results of a program to measure and model the precipitation scavenging of urban pollutants in the St. Louis area. The primary field measurements of the program are of concentrations of trace inorganics in rainwater collected at specific locations in the area. A review of possible field experimental designs in the context of the modeling objectives of this study indicates that the concept of a regional pollution material balance is an appropriate initial approach. The scavenging term in the balance is the scavenging rate, the mass of a given pollutant removed per unit distance along the storm path per unit time. These rates were computed from the concentrations measured during five convective storms in August, 1972. For one storm, where the scavenging rates were determined at three distances from the city, the derived downstorm removal rates for sulfate and nitrate were comparable in magnitude to estimates of the urban area emission rates. Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Precipitation Scavenging Sulfate Nitrate Metropolitan Sources		Meteorology Precipitation Scavenging
18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS (This Report)	21. NO. OF PAGES 14
	20. SECURITY CLASS (This page)	22. PRICE 5.75-2.25

CONTENTS

	<u>Page</u>
ABSTRACT	iv
LIST OF FIGURES	v
LIST OF TABLES	vii
ACKNOWLEDGEMENTS	viii

SECTIONS

I.	CONCLUSIONS	1
II.	RECOMMENDATIONS	2
III.	INTRODUCTION	3
IV.	MODELING OF SCAVENGING BY CONVECTIVE STORMS	7
V.	EXPERIMENT DESIGN	25
VI.	EXPERIMENTAL RESULTS: AUGUST, 1972	37
VII.	ANALYSIS OF RESULTS	63
VIII.	REFERENCES	85
IX.	NOMENCLATURE	87
X.	APPENDICES	91

ABSTRACT

This report describes initial results of a program to measure and model the precipitation scavenging of urban pollutants in the St. Louis area. The primary field measurements of the program are of concentrations of trace inorganics (H^+ , SO_3^{--} , SO_4^{--} , NH_4^+ , NO_2^- , NO_3^-) in rainwater collected at specific locations in the area. These, along with supporting field measurements, will be used to formulate and verify mathematical models of scavenging which will subsequently be employed as components of an overall model developed by the Environmental Protection Agency's Regional Air Pollution Study.

A review of possible field experimental designs in the context of the modeling objectives of this study indicates that the concept of a regional pollution material balance is an appropriate initial approach. The scavenging term in the balance is the scavenging rate, the mass of a given pollutant removed per unit distance (along the storm path) per unit time. These rates were computed from the concentrations measured during five convective storms in August, 1972. For one storm, where scavenging rates were determined at three distances from the city, the derived downstorm removal rates (mass per unit time) for sulfate and nitrate were comparable in magnitude to estimates made of the urban area emission rates.

This report is submitted in fulfillment of work specified in proposal No. 300A00584 (BNW-389), Amendment 4, by Battelle, Pacific Northwest Laboratories, under the sponsorship of the Environmental Protection Agency. Work was completed as of July, 1973.

FIGURES

	<u>Page</u>
1. Simplified Schematic of RAPS Model	4
2. Schematic of Cumulonimbus Cloud	8
3. Wind Shear Structure of Cumulonimbus Cloud	10
4. Updraft and Downdraft Interactions in Cumulonimbus Cloud . .	12
5. Material Balance Schematic for Washout Ratio Analysis. . . .	15
6. Schematic Representation of May's ⁵ Model	19
7. Schematic for Macroscopic Storm Cell Model	21
8. Schematic of Overall Regional Material Balance	26
9. Precipitation Sampling Array: August 1972	30
10. Freezing Precipitation Sampler	33
11. Rainfall Map, Run 1.	42
12. National Weather Service Radar Echo Maps, Run 1	43
13. Radiosonde Results, 1402 CST, August 19, 1972.	45
14. Rainfall Map, Run 2.	46
15. National Weather Service Radar Echo Maps, Run 2	47
16. Radiosonde Results, 0938 CST, August 20, 1972	48
17. Radiosonde Results, 1430 CST, August 20, 1972	49
18. Rainfall Map, Run 3	51
19. Radiosonde Results, 1417 CST, August 21, 1972	53
20. Rainfall Map, Run 4	54
21. National Weather Service Radar Echo Map, Run 4	55
22. Radiosonde Results, 1025 CST, August 25, 1972	57
23. Radiosonde Results, 1501 CST, August 25, 1972	58
24. Aircraft Sounding Results for SO ₂ Air Concentrations, August 16, 1972	60

	<u>Page</u>
25. Rainfall and Rain Pollution Fluxes, Runs 1 and 2	69
26. Rainfall and Rain Pollution Fluxes, Run 3	70
27. Rainfall and Rain Pollution Fluxes, Run 4, Line A	71
28. Rainfall and Rain Pollution Fluxes, Run 4, Line B	72
29. Rainfall and Rain Pollution Fluxes, Run 4, Line C	73
30. Component of the Wind in the Plane of Motion of the Storm as a Function of Height for the 21 August 1972 Storm . . .	79
31. Time Evolution of Maximum Upward Motion (m/sec), Maximum Downward Motion (m/sec), and Maximum Rainwater Mixing Ratio for the Model Storm	81
32. The Motion Field Within the Model Storm as Represented by the Streamfunction (kg/m-sec)	82
33. The Pollutant Distribution at Four Different Times Following its Insertion into the Storm Environment; (Upper left) Time = 0, (Upper right) Time = 30 min, (Lower left) Time = 50 min, and (Lower right) Time = 70 min.	84

TABLES

	<u>Page</u>
1. Convective Storm Properties	9
2. Input Measurements from Field Study	29
3. Analytical Procedures for Rain Chemistry	34
4. General Field Information: August 1972	38
5. Results of Chemical Analyses	39
6. Condensation Nuclei: August 16 Aircraft Sounding	61
7. Sampling Line Average Concentrations: August 1972	65
8. Selected Air Concentrations of Particulate Pollutants for Midwest Cities, and Estimate of Maximum Dry Deposition Flux for $v_d = 5$ cm/sec	68
9. Scavenging Rates: August 1972	75
10. Fractional Removal and Rate of Removal by Scavenging: Run 4, Lines B and C	76
11. Variables of State and Water Vapor Mixing Ratio as a Function of Height Used as Environmental Conditions for Model Calculations. Based Upon Observations Taken at Lambert Field, St. Louis, Missouri on 21 August 1972 at 1417 CST.	80

ACKNOWLEDGMENTS

This research was conducted by scientific and technical personnel of the Atmospheric Sciences Department of Battelle-Northwest Laboratories under related services agreement BNW-389 with the Richland Operations Office, Atomic Energy Commission, for the Division of Meteorology, U. S. Environmental Protection Agency. The following Battelle personnel contributed significantly to this project:

A. J. Alkezweeny	F. B. Steele
J. M. Baily	T. M. Tanner
F. O. Gladfelder	C. W. Thomas
D. W. Glover	N. A. Wogman
M. C. Miller	J. A. Young
J. W. Slood	

Our efforts formed a part of a cooperative effort, the Metropolitan Meteorological Experiment (METROMEX). Other groups in this effort included:

Illinois State Water Survey
University of Chicago
University of Wyoming
Stanford Research Institute
Argonne National Laboratory.

We express our sincere appreciation to these groups for their assistance to this study.

We are also indebted to Mr. George Brancato and his staff at the National Weather Service Station at Lambert Field, for their cooperation and technical interest, which were major factors contributing to the success of this research. In addition, we express our thanks to Mr. Ralph Murkin and the staff at the Lambert Federal Aviation Administration Control Tower for their continued help and cooperation, which were also major elements leading to the successful outcome of this project.

SECTION I.

CONCLUSIONS

The concentration measurements of this study have demonstrated that precipitation scavenging by convective storms can be an extremely effective mechanism for removal of urban pollutants from the atmosphere. Grid-point measurements indicate that spatial concentration distributions of common inorganic pollutants in their higher oxidation states--sulfate and nitrate--show little variability over the scale of a kilometer or more. Substances in lower oxidation states (with the exception of ammonia) tend to exhibit more variability--ostensibly because of greater source-configuration dependence for these constituents.

The data from this study do not provide a simple or obvious assessment of the relative contributions to precipitation chemistry of St. Louis *vs.* "background" contamination. However, concentration--and subsequently, scavenging rate--measurements made at various distances downstorm of the urban area indicate that precipitation scavenging removal rates can be comparable to urban emission rate estimates. The importance of background pollution to this effect, as well as more quantitative explanations of scavenging rates and source magnitudes will be examined in forthcoming modeling efforts of this program.

SECTION II.

RECOMMENDATIONS

This report documents results from two field studies, conducted during the summers of 1972 and 1973. The recommendations following the first of these two studies have been largely fulfilled by the second; we list them here only to provide the reader some perspective to the program:

- In view of our 1972 findings regarding spatial distributions of rainborne pollution, an additional field program should be conducted to expand the data base for the convective-storm component of this study.
- This additional program should have a modified sampler orientation possessing the following characteristics:
 - a) A relaxation of sampler spacing in the cross-storm direction
 - b) A grid orientation, rather than arcs, so that greater down-storm resolution can be obtained
 - c) More samplers closer to the metropolitan core, and
 - d) At least one sequential precipitation sampler.

Field results from the 1973 experiments, which fulfilled these objectives, are summarized in Appendix I of this report.

Additional recommendations arising from these two field investigations are given as follows: First, a frontal-storm scavenging experiment should be conducted in the St. Louis area to provide a RAPS data base similar to that acquired for convective storms. Second, the data that have been collected to date should be evaluated carefully, and examined in the context of the models described in this report. Subsequently these (and possibly additional) models should be evaluated as potential candidates for incorporation in the RAPS model structure. A large fraction of the future program support should be dedicated to this portion of the study to ensure the most beneficial and meaningful utilization of these field results.

SECTION III.

INTRODUCTION

The Regional Air Pollution Study (RAPS) has been initiated by the Environmental Protection Agency with the primary objective of developing comprehensive air quality models for use in support of future emission control strategy. Because of the magnitude and complexity of this modeling problem, the RAPS has been designed to facilitate relatively independent modeling of individual mechanisms of atmospheric response; subsequent combination of these interacting "submodels" will result in the desired comprehensive models as shown by the simplified schematic of Figure 1. Precipitation scavenging is one such submodel within this structure; the objective of the research described in this report series is to formulate reliable precipitation scavenging submodels in accordance with the overall requirements of the Regional Air Pollution Study.

Precipitation scavenging is an important component of atmospheric response both from the standpoint of *delivery* of pollutants to the Earth's surface and from that of *depletion* of these materials from the atmosphere. In modeling local phenomena, the traditional approach has been to neglect the effects of scavenging, noting in the process that the small amounts of depletion involved tend to add a degree of conservatism to calculations of ambient air concentrations. On the scale of the present study, however, scavenging processes tend, on the average, to reduce ambient levels significantly. Here both the spatial and temporal scales are sufficiently large that 1) slower removal processes tend to become significant, and/or 2) complex, efficient scavenging entities such as thunderstorms can completely run their course within the region of study. Thus, it is essential that scavenging phenomena be considered in any comprehensive control strategy that is regional in extent.

The formulation of adequate models to describe precipitation scavenging in a regional situation necessarily involves consideration of a host of pertinent atmospheric processes and variables. These include source

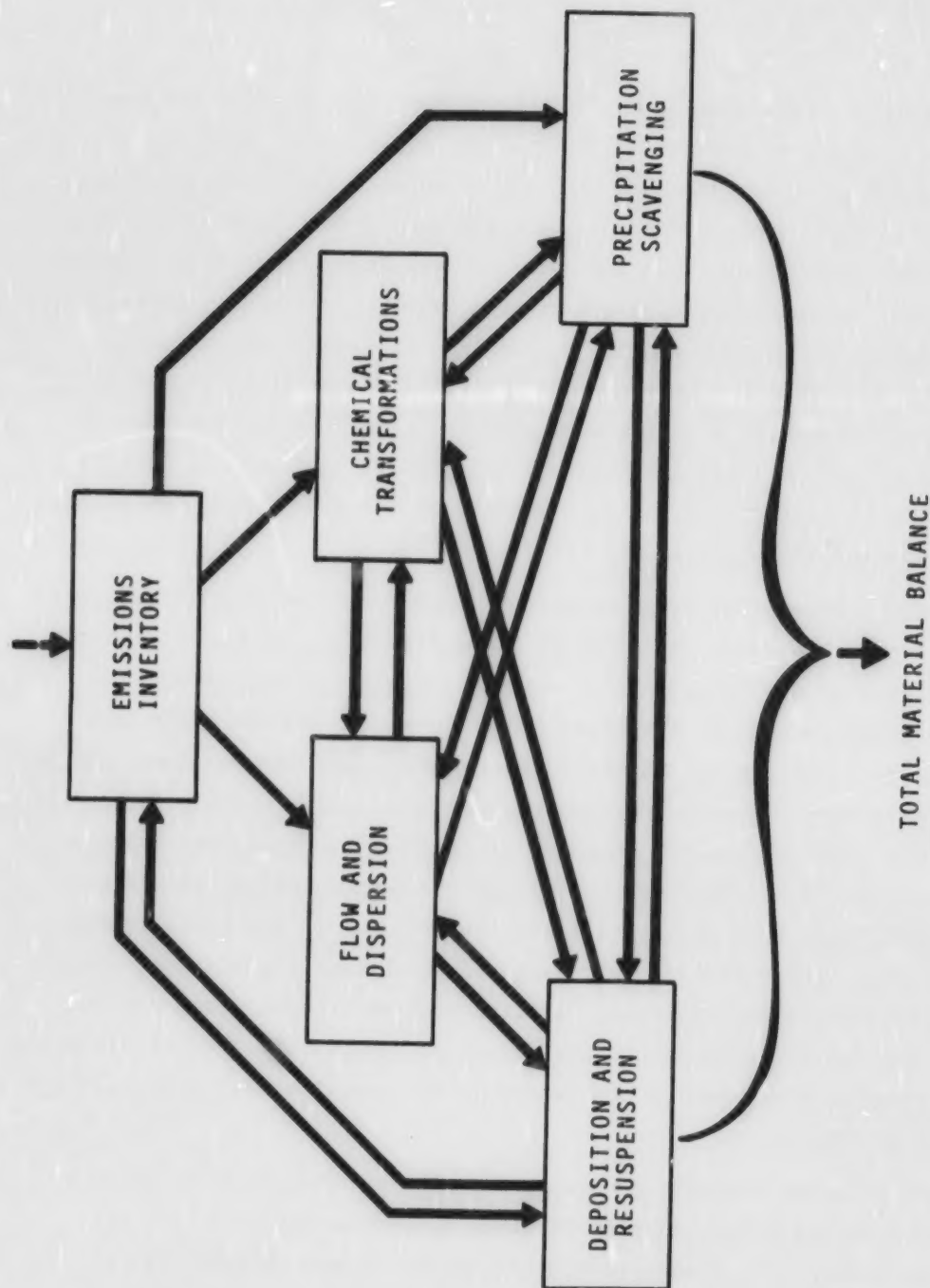


FIGURE 1. SIMPLIFIED SCHEMATIC OF RAPS MODEL.

characteristics and the efficiencies of removal associated with precipitation of various types, whether through simple below-cloud scavenging from pollution-laden air near the ground (washout) or through the more complex process of uptake by storms and subsequent removal - possibly at some place outside the metropolitan area. Precipitation chemistry, precipitation and cloud microphysics, and storm dynamics are all prime factors of consideration. Because of these multiple considerations this program has been organized into individual segments, and a series of reports will be published as the research progresses. The initial research emphasis is on the analysis of scavenging by convective storms; later efforts will focus on frontal-storm activity. Accordingly, the objectives of this initial report of the series are as follows:

- 1) examination of techniques for modeling of scavenging by convective storms and their applicability to RAPS requirements,
- 2) discussion of field experiment design for convective-storm scavenging as it relates to modeling demands
- 3) presentation of field data from the 1972 and 1973 convective-storm field measurement series, and
- 4) presentation of a review of precipitation chemistry as it relates to regional modeling requirements.*

Owing to unanticipated program changes, the 1973 field data are not presented in detail. These are summarized in Appendix A, along with the review of precipitation chemistry which has been included to provide an overview of the current state of the art in this field. The remainder of the above items are presented in the main text of this report.

The St. Louis, Missouri metropolitan area has been chosen as the site of the RAPS field program. This is also the site of the Metropolitan Meteorological Experiment (METROMEX), currently in its fourth year of progress. METROMEX is a cooperative effort of independent research groups working in the St. Louis area to examine urban weather modification effects. While the research described in this report is aimed specifically at RAPS

* This portion of the research effort was supported in part by funding from the AEC Division of Biomedical and Environmental Research.

objectives it is also an interactive component of METROMEX, and many of the supporting measurements utilized in this report have been acquired through cooperative efforts with our colleagues in the METROMEX program.

SECTION IV.

MODELING OF SCAVENGING BY CONVECTIVE STORMS

There are several possible approaches to modeling scavenging by convective storms, and consideration of these is a fundamental prerequisite for field experiment design. We address this problem in the present section by first considering the basic characteristics of convective storms, and then describing possible modeling formulations in the context of their implications with regard to experiment design.

A QUALITATIVE CONVECTIVE STORM PICTURE

Qualitative descriptions of convective storm processes have been presented in the meteorological literature at various times since the latter part of the 19th century.¹ Modifications have come about as more pertinent observations have been gathered, and as refinements in theory concerning cloud dynamics and microphysics have developed which are consistent with these observations. This description will be limited to the case of storms experiencing moderate to strong vertical wind shear in convectively unstable environments, since the best organized storms in the St. Louis area occur under these conditions during the summer months.

The typical dimensions of a thunderstorm (cumulonimbus cloud) are 5 to 30 km in horizontal extent and 10-18 km in the vertical, as shown schematically in Figure 2. Since the freezing level in summertime is usually at the 4 to 5 km level, half or more of the cloud volume consists of ice in various forms. Near the top the water is entirely frozen and an anvil-shaped ice cloud may extend outward from the main portion of the storm for many tens of kilometers in the direction of the strong upper level winds. Near the cloud base, where in one area droplets form in upward moving air and in another area rain falls in downward moving air, the water (except for hailstones) is in the liquid state. Near the freezing level a mixture of liquid droplets, snow, and hail may exist. At increasingly higher levels in the cloud a lesser fraction of the water is in a liquid or supercooled state.

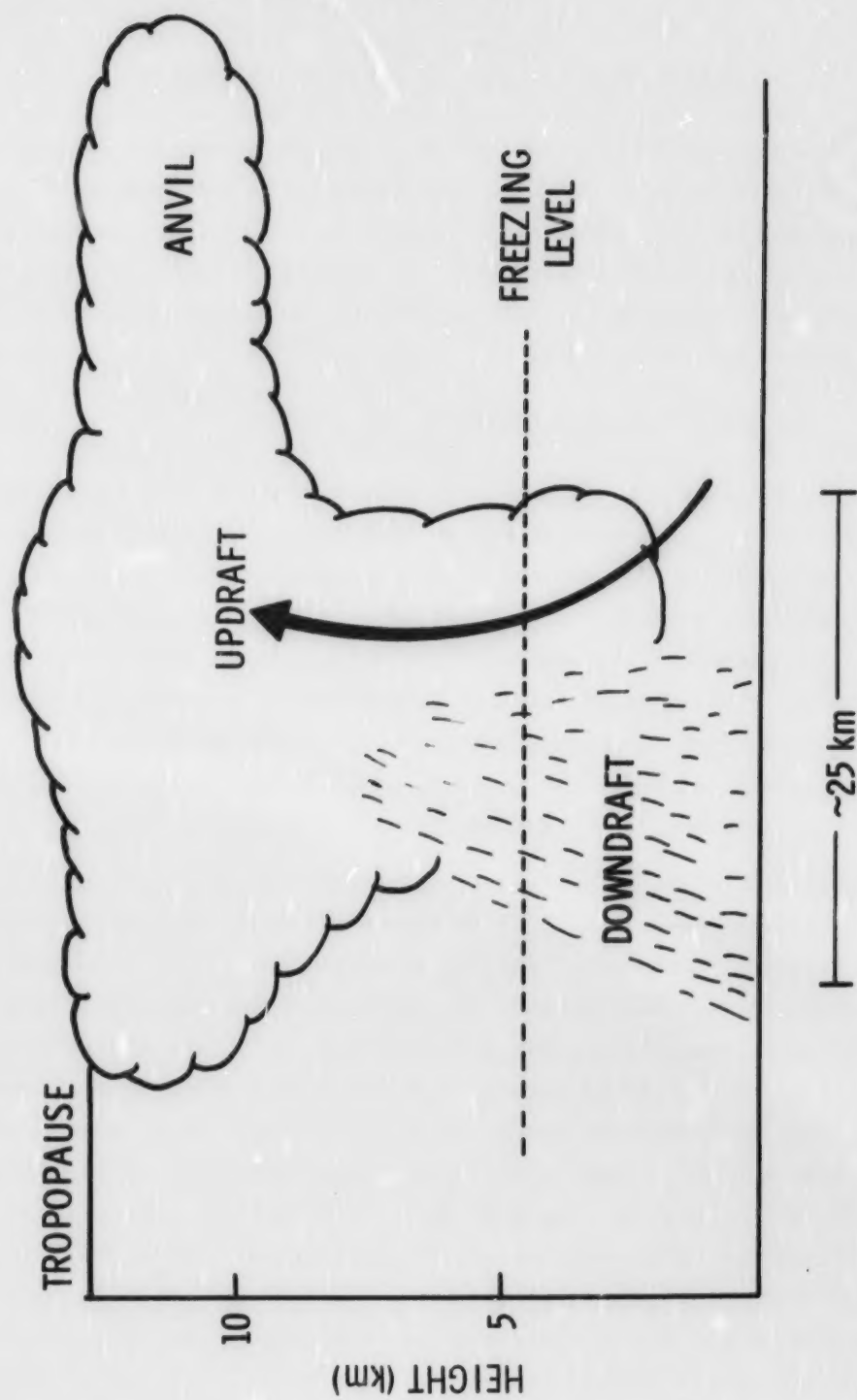


FIGURE 2. SCHEMATIC OF CUMULONIMBUS CLOUD.

Table 1 includes estimates of the maximum warming in the updraft (resulting from the release of latent heat of condensation) and other quantities for both the typical thunderstorm and the large severe storms.

Table 1. CONVECTIVE STORM PROPERTIES

Feature	Average Storm	Severe Storm
Maximum warming in updraft	Few C	10-15 C
Maximum cooling in downdraft (surface)	5-10 C	10-15 C
Maximum updraft speed	10-15 m/sec	20-40 m/sec
Maximum water concentration	5 g/m ³	10-15 g/m ³
Maximum surface wind gusts	10-20 m/sec	20-40 m/sec

The relationship of the motion of these storms to the motion of the environmental air is not often a simple one. Since these storms tend to exist in regions where both the speed and direction of the horizontal wind vary with altitude, the speed and direction of the storm are not likely to be the same as the environmental wind speed and direction at a given altitude. The storms of weak to moderate intensity tend to move at speeds and directions which are approximately the average of the environmental winds through the height of the storm. With the larger, more intense storms, however, the movement is partly translational and partly propagative, and the motion is usually to the right of the mean environmental wind direction and the speed somewhat less. This propagation is due to either a continuous or discontinuous regeneration on the storm's right flank which is closely related to the availability of moisture there.

The reason for the importance of vertical wind shear in combination with convective instability was pointed out by Newton² and is shown schematically in Figure 3. The arrows in the drawing represent the motion of the storm itself and air motions in its environment; the lengths of the arrows indicate relative magnitudes of storm or wind speed. It should be noted that this is a two-dimensional representation in the plane of propagation

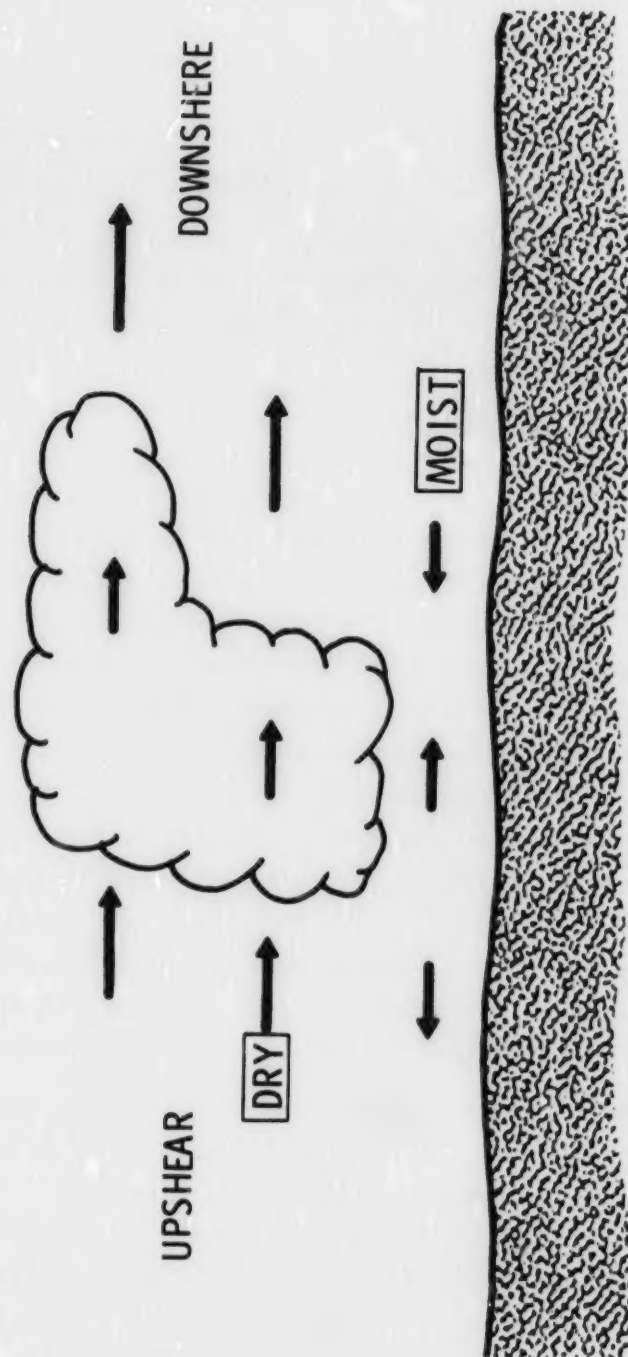


FIGURE 3. WIND SHEAR STRUCTURE OF CUMULONIMBUS CLOUD.

of the storm, whereas real storms are three-dimensional. This consideration, however, does not affect the basic concept to be put forth here. Note that the storm motion is different from that in both low and middle levels as well as high levels, so that new air is entering the storm at various locations. Low level air enters from the right (downshear), but because of the strong vertical shear, middle-level air overtakes the storm from the left (upshear). The low-level air is quite moist, a situation that favors updraft development due to buoyancy produced by condensational warming; the middle level air is quite dry and favorable for downdraft development by means of negative buoyancy produced by cooling, accompanying the evaporation of liquid water. These are the basic driving mechanisms for the conversion of the latent energy of the environment into the kinetic energy of the storm circulation.

There is also a cooperative interaction which occurs between the updraft and downdraft within the storm. Details of this interaction are uncertain, but basic mechanism can be inferred from observations in the storm's periphery. Figure 4 illustrates this interaction, at least in part. The evaporative cooling in the downdraft air produces a "dome" of cold air near the ground which may be 10 C or more colder than the surrounding surface air. This results in a hydrostatically-produced high pressure area in the cold air which is one of three factors tending to accelerate low-level air horizontally in the downshear direction. A second factor is that the air which moves downward in the downdraft must spread horizontally as it nears the ground. A third factor which also may be important in producing strong horizontal motions along the right side of this cold air is the tendency for the transfer of horizontal momentum from middle levels to lower levels by the downdraft. These strong horizontal motions resulting from the presence of the storm encounter the low-level ambient air, producing horizontal convergence near the ground and upward motion at higher levels. The moist ambient air is thus lifted over the cold advancing air to the condensation level, where the release of latent heat allows for further upward penetration of the cloud. The updraft is quite likely tilted from the vertical in an upshear sense from the surface to the mid-troposphere

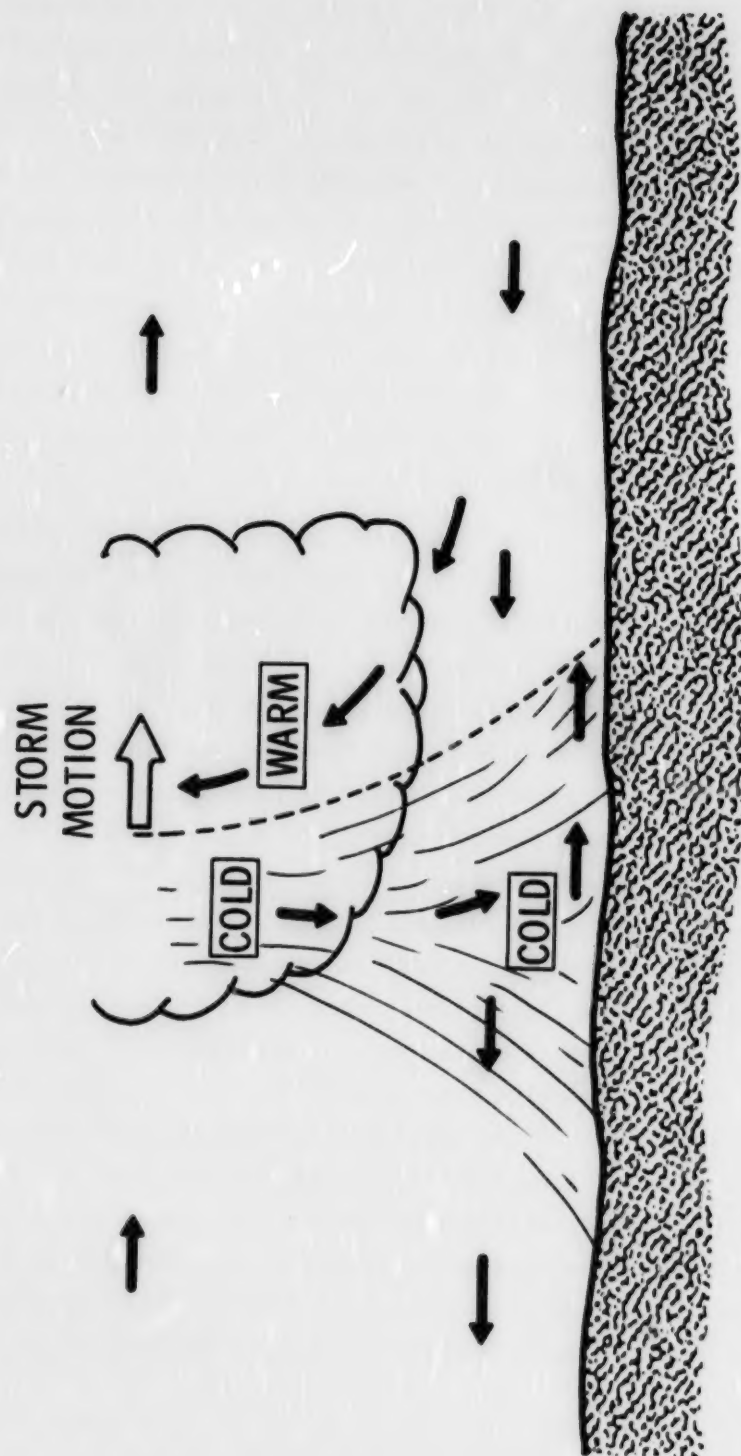


FIGURE 4. UPDRAFT AND DOWNDRAFT INTERACTIONS IN CUMULONIMBUS CLOUD.

so that rain produced in it falls into the downdraft region where it may undergo varying degrees of evaporation. It is in this sense that the updraft and downdraft are dependent one upon the other as was mentioned previously.

With the preceding description in mind, a framework is available for the discussion of convective storm scavenging models and the relation of each to RAPS objectives. Although it seems likely in light of this description that in-cloud scavenging as a result of incorporation of low-level polluted air by the updraft is the dominating scavenging process, not all scavenging models attempt to treat this process explicitly. Therefore in the following section in our discussion of various scavenging models, the above concepts of storm structure are taken into account to varying degrees, depending upon the spatial scale and detail contained within each model.

SCAVENGING MODELS

In reviewing potential modeling techniques for precipitation scavenging prediction and assessment, it is important to note that despite large differences in complexity, resolution, and scale, all such models are formulated from basic material balances; thus it is convenient to categorize models in terms of this common property. Here we itemize and describe briefly some potentially useful modeling approaches in order of increasing complexity. One should note that the approaches described here are certainly not the only ones possible. They do, however, provide a summary of past and anticipated modeling activity that is adequate to illustrate the present discussion of experiment design features.

Empirical-Climatological Approach

As its name implies, this approach to scavenging analysis entails simply the interpretation of wet deposition rates purely on the basis of past behavior. It can be challenged in the present context because it is a model only in the most general sense. It can be described in terms of a gross material balance, however, and related to competing processes in the atmosphere by defining the metropolitan area as a "system" and summing

input and output contributions as indicated later in Figure 5. This gross material balance concept is also useful for experiment design, since the measurements that are pertinent to it tend also to fulfill the requirements of other modeling approaches. This balance will be discussed in further detail in the following section.

Insofar as the prediction of specific concentrations of trace pollutants in precipitation is concerned, the empirical-climatological approach is certainly the simplest, since it involves estimation solely on the basis of past observations. It is also the easiest to interface with the other RAPS submodels, since it requires minimal exchange of information between components of the overall modeling structure.

Washout Ratios

Washout ratio is defined here as the ratio of concentrations of pollutant A in water and in air at ground level:

$$r_w = \frac{\text{mass of A in precipitation/liter precipitation}}{\text{mass of A in air/liter air}} . \quad (1)$$

Engelmann^{3,4} has formulated a simple model to explain the past observations of rather constant washout ratios for a number of substances over wide ranges of conditions. As shown in Figure 5, Engelmann's approach is to perform a macroscopic material balance over a storm or cloud that is assumed to exist in a quasisteady state. Moist, polluted air enters the system from the left, and its water vapor partially condenses. Consequently, a fraction of A is removed from the air and leaves via precipitation scavenging; the remaining fraction leaves in the air exiting the system to the right.

If m_i , m_f , and m_r are the quantities of material entering and leaving the system per unit time, then the material balance is given by

$$m_r = m_i - m_f . \quad (2)$$

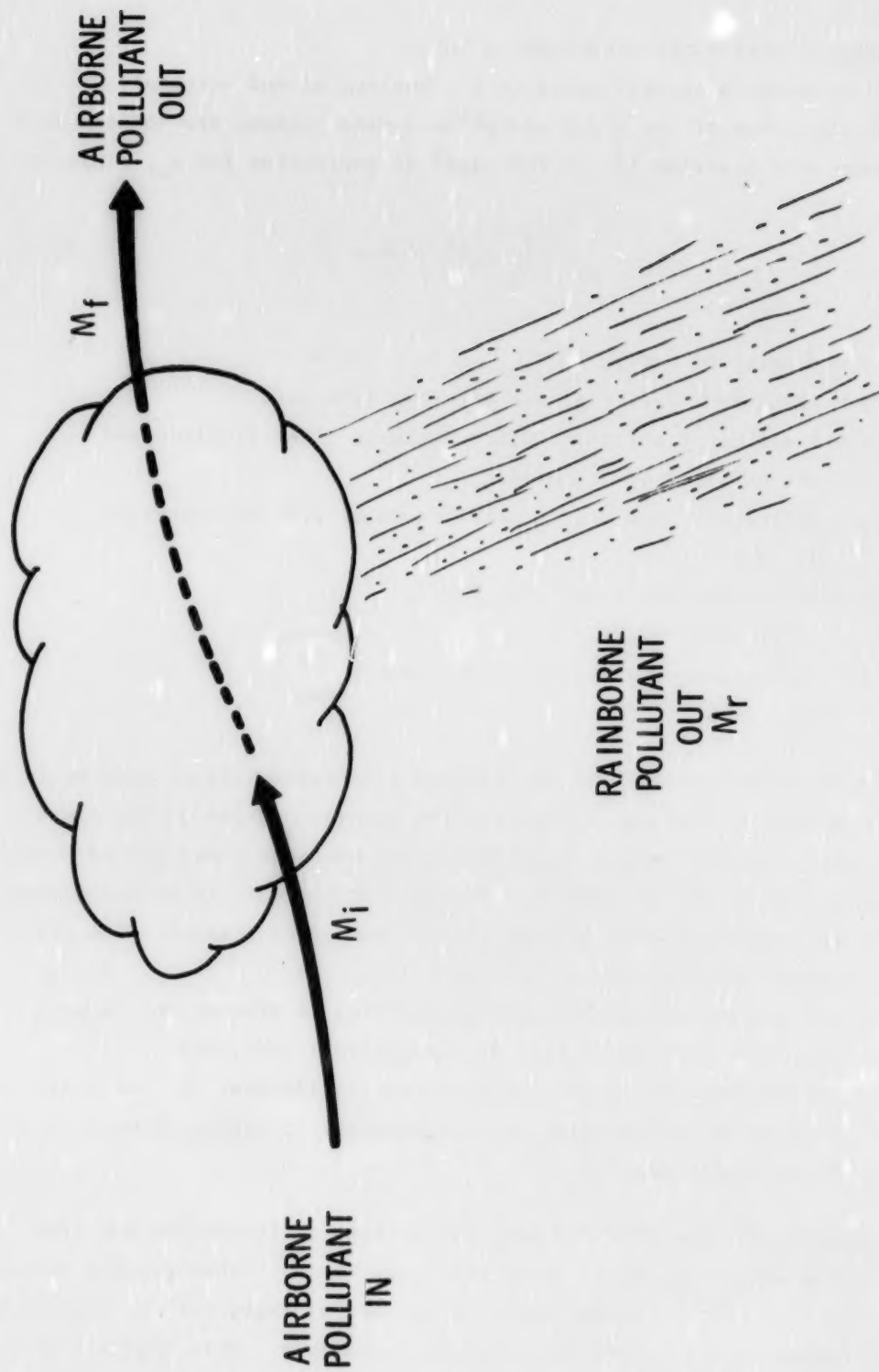


FIGURE 5. MATERIAL BALANCE SCHEMATIC FOR WASHOUT RATIO ANALYSIS.

By making further simplifications--notably:

1) airborne A is well mixed in the horizontal and vertical,

2) the areas of the storm updraft and rain regions are comparable--

Engelmann used Equation (2) to formulate an expression for r_w . This is

$$r_w = \frac{c}{x} = \frac{\rho f}{qE_2} + \frac{(1-n)\rho\beta}{q} + \frac{HA}{J} \quad (3)$$

where ρ = density of water

q = absolute humidity of air entering from left

f = fraction of particles which nucleate cloud droplets and are subsequently removed

E_2 = efficiency of cloud in removing water from air entering at left

β = dimensionless "reactivity factor"

H = cloud base height

Λ = below-cloud scavenging coefficient

J = rain rate.

The use of washout ratios for the RAPS is attractive because here again we require little interchange of information between modules of the overall urban model; in its simplest application one needs only the ground-level concentrations in air to proceed. This model, however, is rather dissatisfying for application at St. Louis for a number of reasons. The two most important of these are:

- 1) its quasisteady state basis is doubtful in view of the large transient effects typical of convective storms, and
- 2) inhomogeneities in the concentration fields near St. Louis are pronounced, in contrast to Engelmann's stipulation of well mixed conditions.

Despite these obvious difficulties, the washout ratio concept may find appreciable use in St. Louis on an empirical basis. Inhomogeneous concentration fields, for instance, possibly may be "averaged out" by employing long duration (e.g., 24-hr) air sampling techniques. This approach will be investigated extensively in forthcoming reports.

Washout Coefficients

In its strictest sense the washout coefficient is simply a transport property. Its concept has been applied so extensively, however, that it often has been tacitly redefined in the context of various models, and at the present time a rather confused state of affairs exists. The true washout coefficient is defined here in terms of a unit volume element in the atmosphere. If k_A is the rate of material A being removed from the gas phase by hydrometeors within this element, then the washout coefficient is defined as

$$\Lambda \equiv \frac{k_A}{\chi_A}, \quad (4)$$

where χ_A is the local gas-phase concentration of A.

This definition can be used to formulate relationships predicting gross removal rates from the air and delivery to the surface. It is important to note, however, *that all such relationships necessitate the use of some type of idealization, or "model" of physical behavior.* An example of this is an approach that has been used frequently in the past. This is to relate the flux of A to the ground in rainwater to a vertical integral of airborne concentration, thus

$$w_A = \Lambda \int_0^\infty \chi_A(z) dz. \quad (5)$$

Such an expression, however, is based on the rather severe restriction of vertical rainfall, as well as a number of additional assumptions. The past tendency to redefine the washout coefficient according to Equation 5, that is,

$$\Lambda = w_A \left(\int_0^\infty \chi_A(z) dz \right)^{-1}, \quad (6)$$

therefore should be regarded with the utmost caution.

A more well-known example of simple modeling using the washout coefficient is May's⁵ method of field analysis. Shown schematically in Figure 6, this method visualizes a plume being emitted from a (point or area) source. The system is assumed to be in a steady state in Eulerian coordinates. It is most conveniently described in a Lagrangian frame of reference, however, by considering a discrete, transient "puff" of the plume as it drifts in the downwind direction. Performing a material balance over this puff of initial mass m_{oA} , one obtains

$$\frac{dm_A}{dx} = - \left(\Lambda m_{oA} / \bar{u} \right) e^{-\Lambda x / \bar{u}} , \quad (7)$$

where m_A is the mass of A at a distance x downwind, and $\bar{u}$ is the mean windspeed. Equating the amount removed from the puff to the amount deposited on the ground gives

$$\frac{dm_A}{dx} = \frac{b}{\bar{u}} \int_{-\infty}^{+\infty} w_A dy , \quad (8)$$

where b is the width of the sampling line in the x direction. Combining Equations (7) and (8), and dropping the exponential term, the expression

$$\Lambda = \frac{b}{m_{oA}} \int_{-\infty}^{+\infty} w_A dy \quad (9)$$

results. This formulation has been used extensively for calculation of Λ from field measurements; in fact, we have employed⁶ the continuous-source variant of this expression,

$$\Lambda = W \frac{\bar{u}}{Q_{oA}} , \quad (10)$$

where Q_{oA} is the pollutant release rate (moles/sec) and W is the scavenging

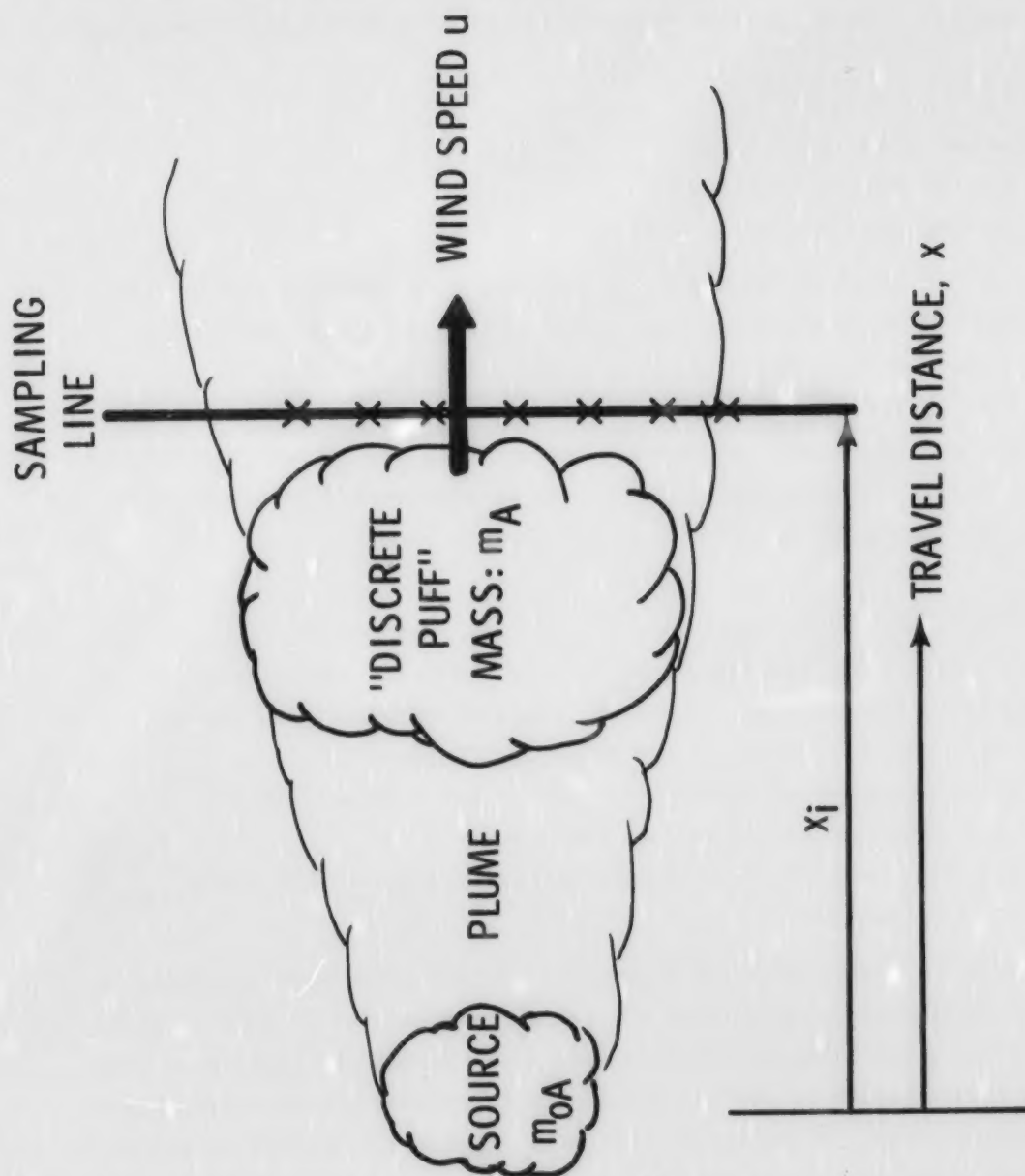


FIGURE 6. SCHEMATIC REPRESENTATION OF MAY'S⁵ MODEL.

rate (defined in Section V) (moles/cm sec), for numerous below-cloud scavenging applications.

The development of the above equations is contingent upon a host of modeling assumptions. These include (but are not restricted to) the assumptions of

- 1) vertical rainfall
- 2) steady state (Eulerian)
- 3) non-meandering plume, and
- 4) no competing removal processes.

In view of this obvious contingency on modeling, one should avoid any tendency to use the above equations to *define* the washout coefficient. This statement applies equally to "rule-of-thumb" definitions--for example, "the washout coefficient is the fractional removal rate." Such statements are unavoidably contingent on modeling assumptions, and a clear distinction between definition and approximation should be preserved in order to avoid confusion in subsequent applications.

Macroscopic Storm-Cell Model

In addition to obvious divergences between the modeling assumptions listed above and anticipated convective storm scavenging behavior, additional problems arise which concern the two following features:

- 1) The propagation of convective cells is not generally in the same direction as the ambient wind, and
- 2) The dimensions of the cells are generally smaller than those of the urban plume.

In an attempt to remedy these shortcomings, we have formulated an additional macroscopic model by performing a material balance over a storm as it transects the urban plume as shown in Figure 7. Details of this model will be given in a forthcoming report. Basically it assumes a quasisteady state storm passing through a varying concentration field. Transients in actual storm characteristics can be incorporated, if desired, by discretizing the quasisteady state system in finite increments along the storm path. Required input to this model--assuming the storm characteristics are known--is simply the environmental air concentration.

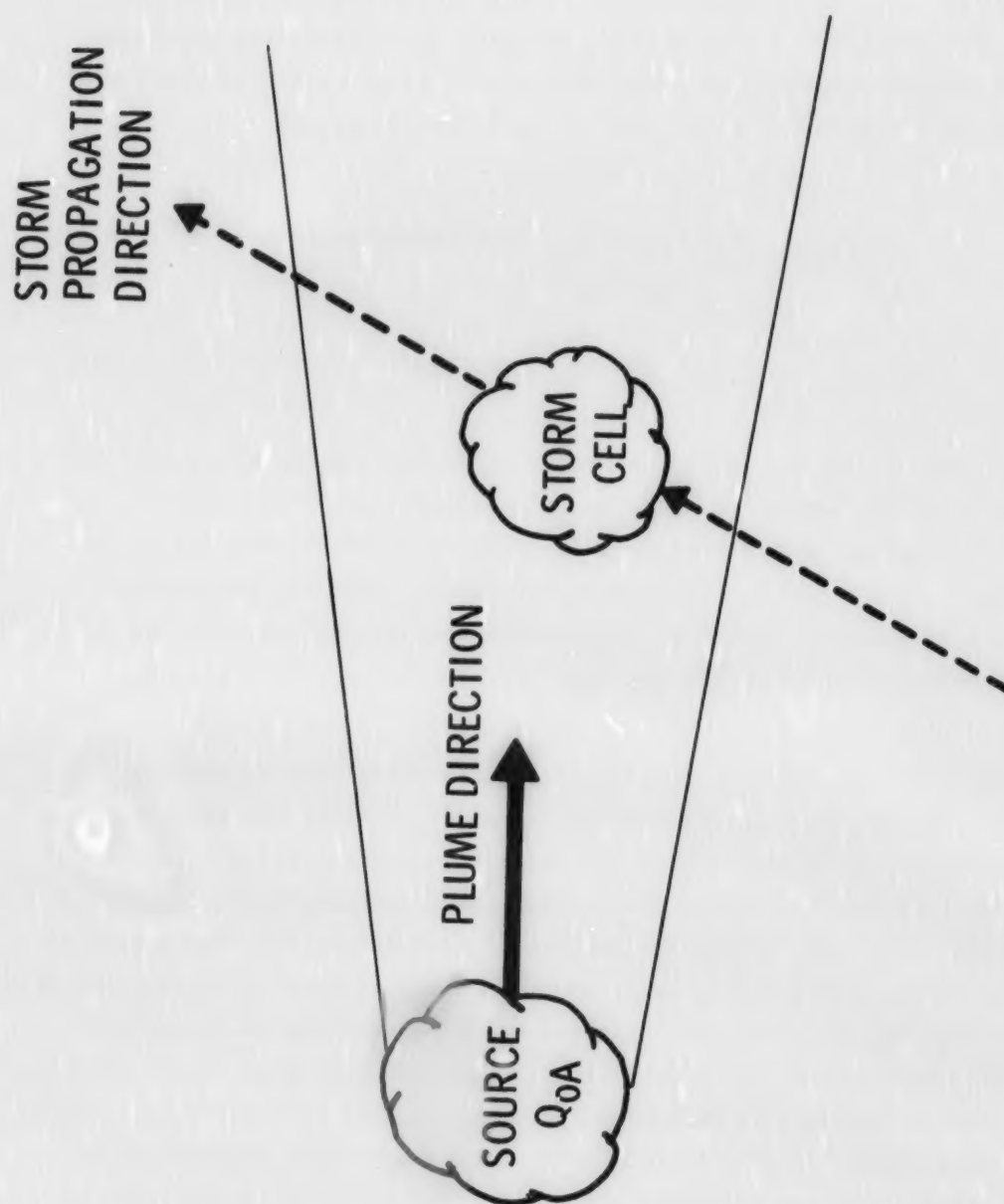


FIGURE 7. SCHEMATIC FOR MACROSCOPIC STORM CELL MODEL.

Microscopic Formulations Describing Scavenging Behavior

Thus far we have concerned ourselves with gross material balances over macroscopic systems. A more refined approach is to formulate and solve the microscopic equations of conservation for pollutant in the precipitation and in the air. In their most general form these are⁷

$$\frac{\partial \rho_{A1}}{\partial t} = -\nabla \cdot \rho_{A1} \bar{v}_{A1} + k_A + r_{A1} \quad (\text{precipitation phase}) \quad (11)$$

and

$$\frac{\partial \rho_{Ag}}{\partial t} = -\nabla \cdot \rho_{Ag} \bar{v}_{Ag} - k_A + r_{Ag} \quad (\text{gas phase}) . \quad (12)$$

Here ρ_{A1} and ρ_{Ag} denote molar densities* of liquid- and gas-phase pollutant A (moles per unit volume of total space) respectively. Similarly $\bar{v}_{A1}$ and $\bar{v}_{Ag}$ denote average velocity vectors for pollutant in the rain and in the gas phase, and r_{A1} and r_{Ag} are the corresponding terms for generation of pollutant by chemical reaction. k_A is defined again as the time rate of loss of pollutant mass in the gas phase by washout, per unit volume of space.

Equations (11) and (12) are coupled to a mathematical description of storm behavior through the velocity vectors $\bar{v}_{A1}$ and $\bar{v}_{Ag}$. Such a description can be provided by storm models obtained by formulating and solving further conservation equations (total mass, water mass, momentum and energy). At the present time such models are capable of calculating the time evolution of air motions, temperature, water vapor, and liquid water distributions in either one, two, or three space dimensions. The one-dimensional models generally concentrate on the details of the cloud microphysics and employ assumptions concerning the dynamics. The two- and three-dimensional models, on the other hand, attempt to deal with the dynamics more realistically while employing parameterization schemes to deal with the microphysics of clouds and rain. In the future with the coming of larger and faster

* Here it should be noted that ρ_{A1} denotes a density of liquid-phase A (moles per unit volume of space) corresponding to an average of the rain-drop ensemble.

computers, detailed microphysics will be included in three-dimensional models and the realism of these numerical experiments will be increased.

Because of the coupling mentioned previously, precipitation scavenging is intimately related to cloud microphysics, and incorporation of Equations (11) and (12) in conjunction with storm models of this type must obviously involve a number of simplifying assumptions. Inclusion of scavenging features in convective cloud models at the present time must be either (a) in detailed form in one-dimensional models or (b) in parameterized form as is the microphysics in two- or three-dimensional models. The relative merits of these approaches depend to some extent upon the type of convective cloud with which one wishes to deal. A small shower cloud existing in an environment whose motion is characterized by very little wind shear might be dealt with fairly realistically in a one-dimensional model. A large isolated thunderstorm on the other hand would probably require a three-dimensional treatment. A possible exception is the well-organized deep convection which occurs in lines which propagate over the earth in a direction roughly perpendicular to the line orientation. The basic aspects of this type convection can be treated rather successfully in two dimensions.⁸

The additional detail of the microscopic approaches necessitates a considerable increase in information to be exchanged between modules within the RAPS scheme. Further aspects of this problem will be discussed in a later section of this report, where initial applications of a two-dimensional storm model to analysis of scavenging by a St. Louis convective storm are presented.

SECTION V.

EXPERIMENT DESIGN

In view of the complexities of convective storms, and the input requirements of models such as those discussed in the previous section, it is convenient to idealize our visualization of the storm somewhat in order to formulate a basis for experiment design. In modeling we are basically interested in material balances of pollution as it is exchanged between the atmosphere, precipitation and the ground surface. Such balances tend to become increasingly complex as finer detail is included regarding spatial and temporal variations; accordingly, the simplest possible such approach is to formulate a macroscopic material balance over the metropolitan complex, as was set forth in Section IV.

This formulation may be accomplished by summing contributions from various pollution sources and sinks as shown in Figure 8. The balance for each pollutant of interest can be stated as follows:

$$\begin{array}{llll} \text{Time rate of change of mass of material} & & & \\ \text{in the system} & = & & \\ \text{Rate of emission to the atmosphere within} & & & \\ \text{system} & + & & \\ \text{Rate of transport to the system by flow} & - & & \\ \text{Rate of transport from the system by} & & & \\ \text{flow} & + & & (13) \\ \text{Rate of gain of material in system by} & & & \\ \text{chemical and microphysical reaction} & - & & \\ \text{Rate of loss of material from system} & & & \\ \text{by dry deposition} & - & & \\ \text{Rate of loss of material from system} & & & \\ \text{by precipitation scavenging} & . & & \end{array}$$

Mathematically, this corresponds to the equation

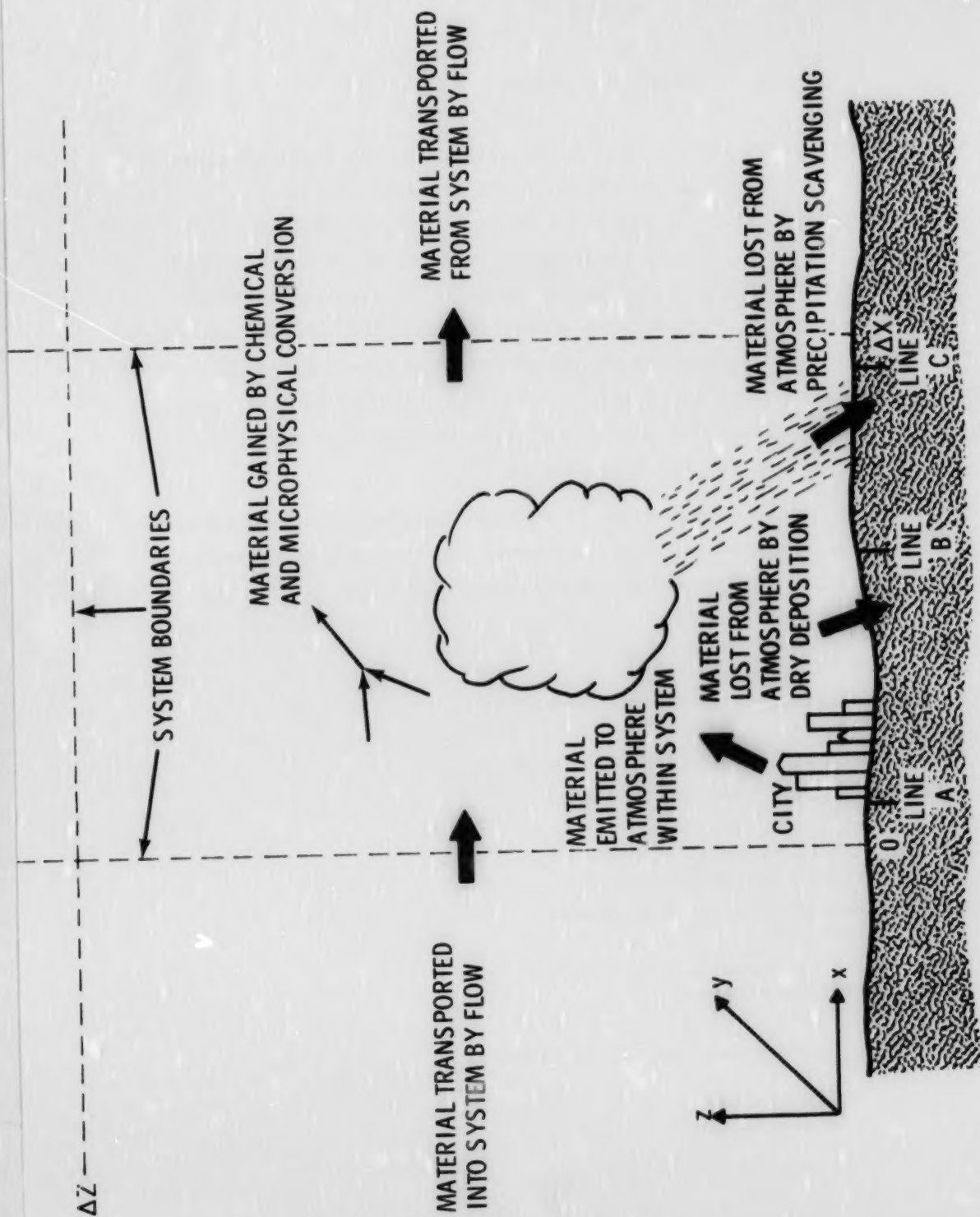


FIGURE 8. SCHEMATIC OF OVERALL REGIONAL MATERIAL BALANCE.

$$\begin{aligned}
\Delta x \Delta y \Delta z \frac{\partial x_A}{\partial t} = & \int_0^{\Delta y} \int_0^{\Delta x} Q_{OA} (x,y) \partial x \partial y + \\
& \int_0^{\Delta z} \int_0^{\Delta y} x_A v_{Ax} \partial y \partial z \Big|_{x=0} + \int_0^{\Delta z} \int_0^{\Delta x} x_A v_{Ay} \partial x \partial z \Big|_{y=0} - \\
& \int_0^{\Delta z} \int_0^{\Delta y} x_A v_{Ax} \partial y \partial z \Big|_{x=\Delta x} - \int_0^{\Delta z} \int_0^{\Delta x} x_A v_{Ay} \partial x \partial z \Big|_{y=\Delta y} - \\
& \int_0^{\Delta y} \int_0^{\Delta x} x_A v_{Az} \partial x \partial y \Big|_{z=0} + \int_0^{\Delta y} \int_0^{\Delta x} x_A v_{Az} \partial x \partial y \Big|_{z=\Delta z} + \\
& \int_0^{\Delta z} \int_0^{\Delta y} \int_0^{\Delta x} r_A (x,y,z) \partial x \partial y \partial z - \\
& \int_0^{\Delta y} \int_0^{\Delta x} d_A (x,y) \partial x \partial y - \int_0^{\Delta y} \int_0^{\Delta x} w_A (x,y) \partial x \partial y . \quad (14)
\end{aligned}$$

where

x_A = air concentration of pollutant A (mass/volume)

Q_{OA} = emission rate of A (mass/area·time)

v_{Ai} = velocity of A in gas phase in i th direction

r_A = generation rate of A by reaction (mass/volume·time)

d_A = dry deposition flux of A (mass/area·time)

w_A = scavenging flux of A (mass/area·time), and

$\Delta x, \Delta y, \Delta z$ = dimensions of systems.

Equation (14) actually corresponds to the basis for a comprehensive RAPS model as depicted in Figure 1; the primary concern of this research project is restricted to the elucidation of w_A , the precipitation scavenging flux. Because of w_A 's dependence on other features of the total material

balance, however, each of these entities must be considered--both from the standpoint of formulating a meaningful experiment design and from that of ensuring that the submodels developed will be of maximum use as modules in an interactive system.

Proceeding with the macroscopic material balance approach, it is obvious that no reasonable field experiment can be designed which could accurately "close" the material balance of Equation (14). Accordingly, we have emphasized direct measurement of scavenging fluxes in this program through use of a precipitation sampling array, but also have included limited support operations which, in conjunction with data obtained from other sources, allow approximate material-balance information to be obtained for scavenging analysis. Table 2 provides a summary of these sources of information.

In addition to the variety of simplifying assumptions and approximations necessitated by this approach, some idealization of storm characteristics is also desirable. The preferred storm for study, for example, would be a single-cell convective disturbance which traverses the city and sampling lines on both sides of town without substantial changes in the storm's character. Such behavior would allow a rather direct comparison of pre- and post-city washout rates, and would simplify other aspects of the material balance considerably. It is obvious that actual storms rarely exhibit such behavior, but experimental data derived from a number of storms will be useful in assessing the variabilities in scavenging behavior as the storms deviate from the ideal in different respects.

The precipitation sampling array for the 1972 field series is shown in Figure 9. The washout flux w was determined at each sampling station via chemical analysis of the collected rainwater. The spatial array of the samplers then dictated the extent to which the total rate of scavenging removal--the last term on the right of Equation (14)--could be evaluated. Resource and personnel limitations did not allow an extensive gridwork in both the x and y directions, so we opted to evaluate the integral in the y direction, normal to the expected direction of storm movement. Thus the array took the form of lines of samplers, and the cross-plume integrated flux, which we shall refer to subsequently as the scavenging rate, is

Table 2. INPUT MEASUREMENTS FROM FIELD STUDY.

Material Balance Component or Meteorological Parameter	Source of Information
x_A	St. Louis Air Pollution Control District Network Illinois EPA network CAMP station Limited aircraft sampling (Battelle & ISWS)
v_{Ai}	Balloon soundings (Battelle & others)
Q_A	Emissions Inventory (EPA)
d_A	Estimation and dustfall measurements
Storm characteristics & trajectory	NWS radar (Lambert field) ISWS radar (Pere Marquette) METROMEX flights
Rainfall pattern	Battelle precipitation chemistry array ISWS raingauge network
Temperature, R. H.	Balloon soundings (Battelle & others) Aircraft data
r_A	<u>Virtually no direct input.</u> Some indi- rect estimations possible by observa- tions of concentration ratios in rain and in air. Note literature survey in Appendix II.
w_A	Comprehensive precipitation chemistry array--major measurement emphasis of this study.

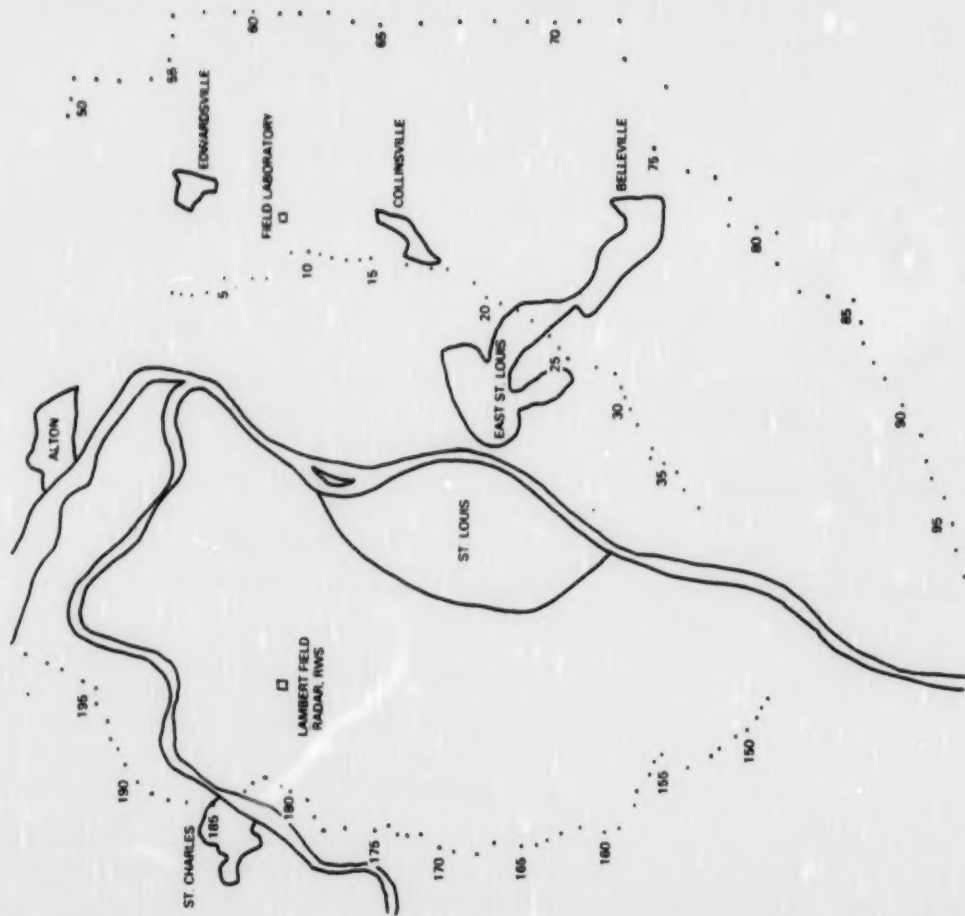


FIGURE 9. PRECIPITATION SAMPLING ARRAY: AUGUST 1972.

$$W \equiv \int_0^b w(x,y) dy \approx 1/2 \sum_{i=1}^{n-1} (c_{ri} J_i + c_{r(i+1)} J_{i+1}) |y_i - y_{i+1}| \quad (15)$$

where n = the total number of collectors along the line

c_{ri} = the concentration mass of pollutant at the i th collector along the line, moles/l

J_i = rainfall rate at i th collector, cm/sec

y_i = the coordinate of the i th collector, cm.

The expected motion of storms was generally from northwest to southeast, so one line was placed upstorm (Line A--numbers 147-200), and two lines were placed downstorm (Line B--numbers 1-38--and Line C--numbers 49-97). The upstorm line was included for measurement of background fluxes.

A proper evaluation of W requires that the sampling line contain the y -direction "extent" of the scavenging. There can be two interpretations of this extent, depending on the type of storm encountered. If the storm is smaller than the breadth of the city, the containment must be of the rainfall (the pollution source is then presumably only part of the city). In the case of more widespread rain, the containment must be of the downstorm projection of the city. These considerations required that the sampling lines be at least as long as the width of the city, but also that the spacing be fine enough so that there be proper scavenging resolution of smaller showers. A compromise was reached whereby the sampler spacing was set at about 1 km (on the assumption that significant showers would be at least kilometers wide) on the inner lines, and about 2 km on the outer line. Since only one field worker was assigned to each line, the complete line (containing more than the y -direction projection of the city) could not be set out on short notice. Consequently we deployed samplers only over selected segments of the lines, and relied on storm forecasting to select which portions of the lines to deploy. During the latter portion of the experiment series, we doubled the sampling spacing, as it appeared that most rains would be extensive.

A special precipitation collector was required for this study because of the desire for chemical analysis of a number of pollutants. Furthermore, the pollutants varied widely in chemical state, reactivity, and sensitivity to post-collection conditions. In the past we have chemically fixed the pollutants at the time of collection, but this required separate collectors for each pollutant and its particular fixing agent. This has been fraught with technical difficulties, and in the present study we attempted to fix the pollutants on collection in single samplers using a freezing technique. It is well known that extremely small amounts of pollutants tend to deposit on the walls of rain collectors unless they are fixed in the ice structure. To a degree this was important in the present study, but we were dealing mainly with larger concentrations. Our main concern was with chemical deterioration, such as conversion of NO_2^- to NO_3^- or desorption of SO_2 or the ammonium ion in the form of NH_3 .

A sampler was designed which would freeze rainfall as it was collected, and which would remain effective in the field for several hours after deployment. The sampler, shown in Figure 10, consists of a 500 ml plastic bottle attached to a 20 cm diameter funnel. In operation this arrangement was enclosed in a Styrofoam insulating container with about 1 kg of dry ice. Thus with deployment of only one sampler and subsequent recovery of one rain sample at each position, we could analyze for all the desired pollutants. Bottle capacity corresponded to about 2 cm of rainfall; in the few cases of rainfall exceeding this amount, estimates were made of amounts up to an additional 2 cm from observation of the level of water in the funnel.

Rain samples were kept frozen until just before chemical analysis, which was completed generally within a few days at the Battelle mobile air pollution laboratory, located at Glen Carbon, Illinois. Some of the samples from the later runs were packed in dry ice and flown to Richland, Washington for analysis after the conclusion of the field trip.

The chemical constituents of the samples which were determined were: pH, SO_2 , $\text{SO}_4^{=}$, NO_2^- , NO_3^- , and NH_4^+ . The first was determined through standard pH technique, the rest by wet chemical methods, using Technicon Autoanalyzers.

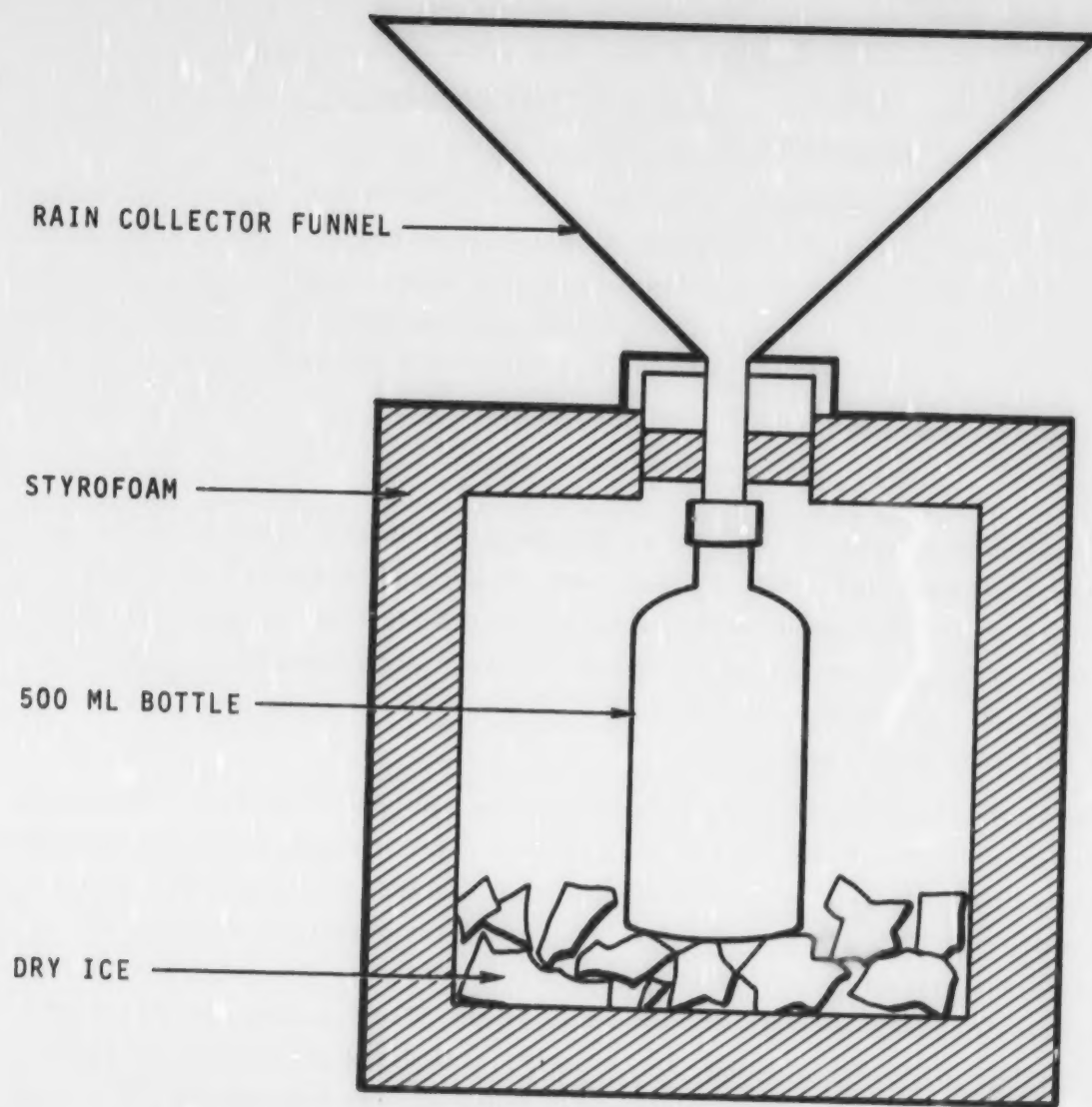


FIGURE 10. FREEZING PRECIPITATION SAMPLER.

A summary of the species examined and the analytical methods used is given in Table 3.

Table 3. ANALYTICAL PROCEDURES FOR RAIN CHEMISTRY.

Species	Analytical Procedure
H^+ (pH)	Glass electrode
SO_2 (dissolved)	Modified West & Gaeke method ⁹
$SO_4^{=}$	Methylthymol blue method ¹⁰
NO_3^-	Phenoldisulfonic acid method ¹⁰
	Chromotropic acid method ^{11, 12}
NH_4^+	Phenoldisulfonic acid method ¹⁰
NO_2^-	Saltzman method ¹³

The samples which were returned to Richland, Washington, were subjected to repeat nitrogen pollutant analyses, both as a check on initial procedures and as a limited evaluation of potential post-collection changes. In addition, an independent method of nitrate analysis was performed as a check on the nitrate procedure. The results of these reanalyses and discussion of errors appears in Section VII.

The general process of conducting scavenging runs was as follows. The field director, stationed at the National Weather Service radar station at Lambert Field, assessed the run potentials for each day and coordinated all activities. When the early morning forecast called for potential showers, the field workers were alerted; if rain appeared imminent, they were advised to prepare the samplers with dry ice, and, if the likely motion and extent of rain were reasonably certain, set out over a directed portion of the sampling lines. The radar observations were necessary for forecasting, it turned out, because it was generally impossible to tell by visual observation from the east side of the city whether or not a shower was coming until the onset of lightning, or obscuration of sunlight. This was because of the poor

visibility attributable to the general high pollution level over the city during the experiment period. After set out of the samplers and evidence that rain had fallen on the sampling lines, collection was instituted at the discretion of the field workers, and the samples were put in frozen storage.

SECTION VI.

EXPERIMENTAL RESULTS: AUGUST, 1972

During the field experimental period--August 8-31, 1972--precipitation was collected on five convective storm days. In addition, radiosondes were flown--attempts were made on all storm days, but flights on other days were also accomplished in support of METROMEX activities--and near-continuous meteorological monitoring was maintained at the National Weather Service station at Lambert Field. Table 4 is a summary of these activities, and Table 5 is the complete list of precipitation sample pollution concentrations. Further discussion of the concentrations is centered in Section VII; the following is a summary of the meteorological and sampling situations for the scavenging runs, plus a brief presentation of aircraft results. All times mentioned are Central Standard, and "STL" is the designation of the weather station at Lambert Field.

RUN 1 (August 12, 1972)

At 0600 a stationary front was located across the Great Lakes, northern Illinois and central Iowa, with a short wave trough at 500 mb over eastern Missouri and Illinois moving slowly eastward as it deepened. A line of showers oriented east-west moved across the St. Louis area from north to south as an apparent squall line. Thunder was reported at STL from 0937-1000, and light showers occurred until 1143. The total rainfall at STL was only 0.05 cm, but radar estimates indicated cloud tops to 12 km before and during passage of the line over the city. One cloud top was noted to 14 km at 1040 some 75 km east-southeast of STL. A rather intense cell passed over sample Line B between 0840 and 1040.

On this day, laboratory and sampling line setup was still underway, with Line C not having been established. The early arrival of rainfall precluded setout of samplers on Line A, but the southern portion of Line B was deployed beginning at 0900. Figure 11 is a map showing the precipitation amounts which fell during the sampling time, and the locations of

Preceding page blank

Table 4. GENERAL FIELD INFORMATION: AUGUST, 1972.

Date	Run No.	Sample Line	Position Numbers ^a	Inclusive ^b Collection Time (Time of Day-CST)	Approximate Storm Path	Rawinsonde Release Time (CST)
8/12/72	1	B	19-38	0912-1433	NW to SE	
8/17/72						1026
8/19/72	2	B	22-28	1421-1647	NW to SE	1402
8/20/72	3	C	61-74	1334-1700	NE to SW	0938, 1430
		B	1-5	1349-1649	NE to SW	
		A	146-153	1530-1840	NE to SW	
8/21/72	4	A	146-190	1530-2030	NW to SE	1417
		B	15-37	1455-1731	NW to SE	
		C	65-89	1503-2001	NW to SE	
8/25/72	5	A	154-168	0955-1705	W to E	1025, 1501
8/28/72						1053

^aSample positions used at which measureable rain fell.

^bTotal time from first collector out to last collector in.

the active sampling positions. The rainfall data on this map and subsequent similar ones were those recorded on the Illinois State Water Survey precipitation array, which consists of over 200 recording rain gages covering an area somewhat larger than our map area.

Radar observations of movement of peak echo intensity indicate that the cell which affected Line B moved from about 320 degrees at about 30 km/hr. The origin of the cell appeared to be roughly over the central business district of St. Louis, with sampling positions 25-35 ostensibly most affected by the city's plume. Figure 12 is an hour-by-hour illustration of National Weather Service radar echo patterns during the time of Run 1 sampling.

Table 5. RESULTS OF CHEMICAL ANALYSES

Date	Run	Position	Rainfall, ^a mm	Concentration ^b (g-moles/l) x 10 ⁶				
				NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺	SO ₄ ⁼
8/12/72	1	22	3.42	.063		18.1	166	44.0
		23	2.09	.059		24.7	141	47.1
		24	1.49	.056		27.2	174	60.9
		25	3.18	.047		14.9	200	47.1
		26	1.45	.243		21.7	120	46.0
		27	.82	.502		6.78	58.9	60.1
		28	.88	.028		6.78	115	31.3
		29	.60	.313		9.06	97.7	20.8
		30	.63	.046		12.6	102	26.7
		31	.69	.583		13.8	55.0	26.4
		32	.62	.039		17.3	129	28.3
		33	.58				33.1	56.7
		34	.68				100	47.1
		35	.66	.067			132	46.7
		36	.72			30.9	45.7	37.8
		37	1.26	.074		16.8	132	35.8
		38	2.06	.074			129	29.3
8/19/72	2	22	.57	1.07			2.00	183
		23	1.09	1.04	161	46.3	1.23	261
		24	2.79	.086	104	40.6	42.7	143
		25	4.54	.065	93.5	23.4	209	108
		26	2.02	.022	123	21.7		136
		27	.26	.239			245	183
		28	.15				25.1	183
8/20/72	3	1	12.8	.087	146	44.4	182	133
		2	8.08	.087	154	55.6	214	164
		3	1.37	.087	206	99.4	170	219
		4	.06					
		5	.35	.109			112	173
		61	.23					230
		62	.20					297
		63		.783				257
		64	.86	.043			153	109
		65	.28	.065			224	163
		66	.06					
		67	.15					
		68	.18					286
		69	.57	.850			10.7	149
		70	9.09	.021	20.2	49.6	93.3	29.1
		71	16.6	.043	49.6	31.2	77.6	35.6
		72	18.2	.043	44.4	22.7	107	25.4

Table 5 (continued). RESULTS OF CHEMICAL ANALYSES

Date	Run	Position	Rainfall, ^a mm	Concentration ^b (g-moles/l) x 10 ⁶				
				NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺	SO ₄ ⁼
8/20/72	3	73	22.8	.021	49.4	26.4	135	53.5
		74	9.89	.021	89.8	24.4	191	91.1
		146	.03					
		147	1.3	.196	229	68.3	95.5	233
		148	6.5	.065	132	52.9	282	186
		149	11.0	.086	123	50.2	178	126
		150	9.8	.130	169	52.4	70.8	261
		151	11.3	.196	157	44.7	251	144
		152	6.2	.086	123	40.1	158	117
		153	3.4	.152	157	62.2	229	167
8/21/72	4	15	1.4	1.96			21.4	158
		17	1.6	1.43	130	9.06	38.0	147
		18	9.8	.174	130	39.6	38.9	130
		19	14.0	.087			126	21.6
		21	10.0	.065	77.6	27.2	191	99.8
		23	5.4	.283	97.7	14.9	9.55	103
		25	27.0 ^c	.043	31.2	33.3	138	89.6
		27	42.0 ^c	.043	99.5	14.7	115	143
		29	59.0 ^c	.021	52.7	28.7	93.3	69.0
		31	56.0 ^c	.065	43.2	27.2	112	50.7
		33	52.0 ^c	.043	43.8	27.9	72.4	51.4
		35	49.0 ^c	.587	36.1	21.4	5.75	48.5
		37	44.0 ^c	.870	50.6	19.3	12.6	175
		65	1.6	.152	79.5	5.31	77.6	93.4
		67	1.3	.086	92.8	20.2	61.7	99.2
		69	1.4	.978	109	9.06	0.95	133
		71	3.1	.086	93.9	20.2	162	127
		73	4.7	.065	71.5	25.4	11.2	77.0
		75	11.5	.021	67.5	10.9	69.2	42.5
		77	12.7	.021	48.8	17.3	60.3	32.5
		79	15.8	.021	37.2	18.6	40.7	16.5
		81	22.0 ^c	.043	34.9	25.4	46.8	
		83	17.0 ^c	.021	33.8	25.2	44.7	27.8
		85	11.9	.065	35.7	43.3	75.9	34.9
		87	2.9	.043	47.0	14.2	132	41.5
		89	1.5	.043	54.2	19.3	91.2	32.9
		146	.7	.043			58.8	63.8
		148	.7	.217			15.8	56.8
		150	.7	.043			60.3	53.1
		152	.8	.522			40.7	47.7
		154	2.3	.543	42.0	10.2	56.2	30.1
		156	1.8	.043	49.8	10.2	115	51.1
		158	2.0	.043	43.5	5.17	158	65.2
		160	3.2	.065	35.5	14.9	83.2	52.4

Table 5 (continued). RESULTS OF CHEMICAL ANALYSES

Date	Run	Position	Rainfall, ^a mm	Concentration ^b (g-moles/l) x 10 ⁶				
				NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺	SO ₄ ⁼
8/21/72	4	163	4.6	.065	46.1	22.7	66.0	39.4
		165	1.4	.065	70.6	17.7	89.1	67.3
		167	2.0	.043	74.3	37.4	70.8	70.4
		169	3.1	.043	49.8	16.6	87.1	47.6
		171	1.8		48.6	32.2	74.1	73.4
		173	0.6	.109			58.8	115
		175	0.15					
		176	0.4	.761			5.25	120
		178	0.06					
		180	.1					
		182	.15					
		184	5.4	.478	34.3	13.3	45.7	32.5
		185	10.6	.283	41.8	12.3	3.80	26.7
		186	3.45	.609	52.4	22.2	29.5	53.3
		188	2.4	.898	92.1	32.2	33.9	60.5
		190	1.1	.870	84.5	23.7	14.4	60.0
8/25/72	5	154	.3	.283			50.1	114
		156	.3	.043			55.0	94.6
		158	.3	.065			40.7	62.1
		160	.3				2.45	79.7
		163	.3	.021			135	42.3
		165	.7	.152			39.8	28.1
		167	.8	.043			58.9	31.3
		168	.8	.021			42.7	32.0

^a Calculated from volume of water collected by sampler.^b All SO₂ concentrations were insignificant.^c Estimated from Illinois State Water Survey raingage records.

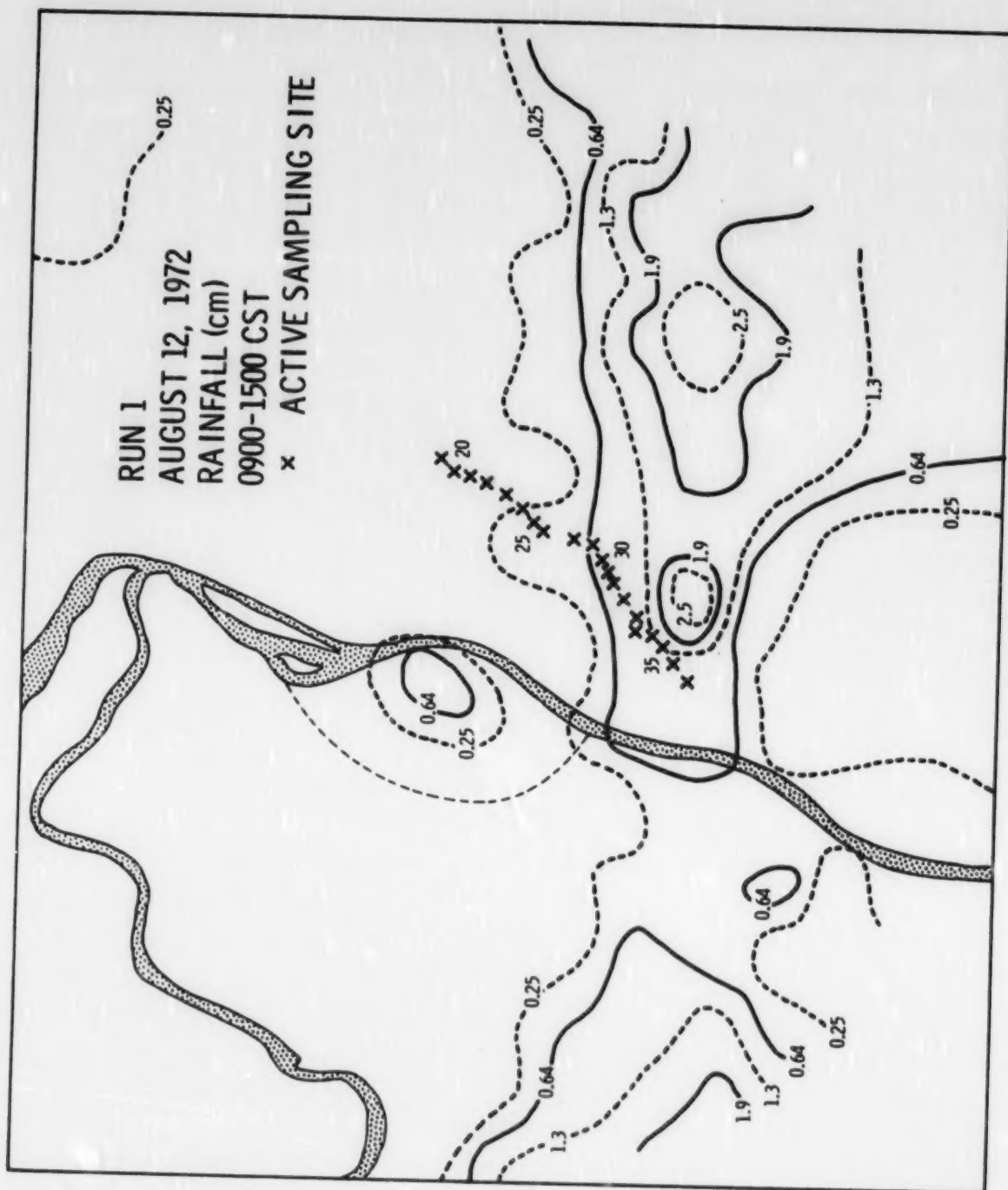


FIGURE 11. RAINFALL MAP, RUN 1.

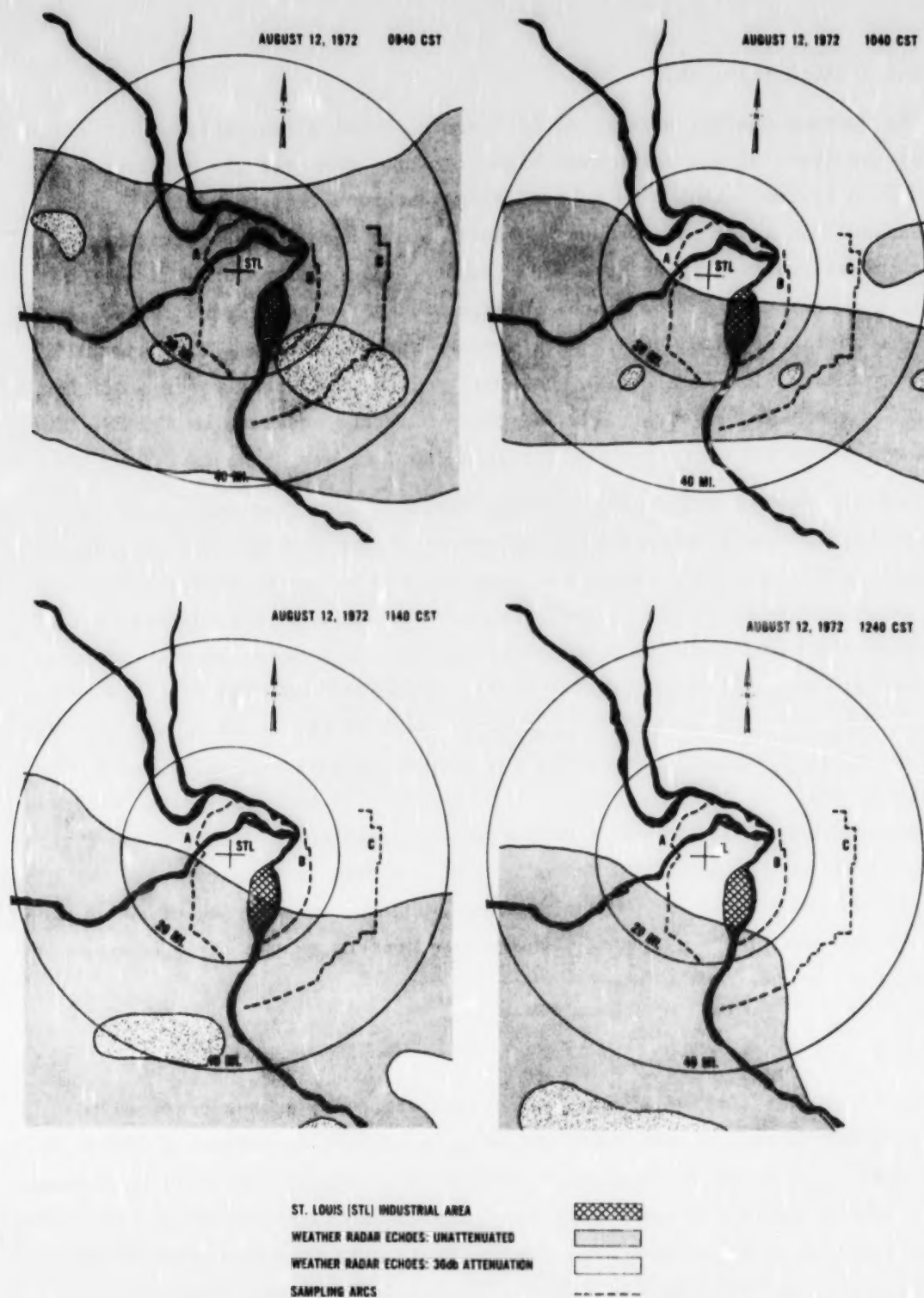


FIGURE 12. NATIONAL WEATHER SERVICE RADAR ECHO MAPS, RUN 1

RUN 2 (AUGUST 19, 1972)

The surface weather pattern at 0600 again showed a stationary front north of the area, with a large weak high pressure area over the entire eastern United States. At 500 mb a broad ridge extended from the Gulf to central Canada. No radar echoes appeared until about noon. The afternoon situation was typified by an apparently random cell development with most cells in the area moving from about 290 degrees. A few persistent cells passed both north and south of STL with thunder reported between 1348 and 1415. No precipitation fell at STL, however, nor on the setout portion of Line A. The radiosonde flight at 1402 indicated moderate moisture to 400 mb. The temperature and wind profiles for this sounding are shown in Figure 13.

Inasmuch as most cells were building rapidly and rather shortlived, a section of Line B approximately downstorm of the city was set out, beginning about 1400. The downstorm personnel doubled up to expedite this setout. Figures 14 and 15 indicate that the sampled cell matured to the south and east of the deployed area; however, only seven of the rain collectors had measurable amounts--those from a trailing edge of the shower. Any rain that occurred on the positions south of Number 28 apparently fell just prior to setout. Thus, the containment achieved was of a small side shower trailing the main storm. The direction of movement of the cell was approximately 305 degrees; thus the sampled rain would appear to be directly downstorm of the city. The origin of the cell is uncertain, as the cloud buildups were rapid and randomly placed, and the time series of radar photographs contains some gaps. The speed of motion of the major echo was about 35 km/hr.

RUN 3 (AUGUST 20, 1972)

The synoptic situation at 0600 was characterized by a wave centered in North Dakota with a cold front extending southward to eastern Colorado and a stationary front southeastward through Iowa and Illinois, and to Alabama. The latter later provided "back door" frontal activity, touching off a line of thunderstorms moving across the St. Louis area from northeast to southwest. Radiosondes taken at STL at 0938 and 1430--Figures 16 and 17--

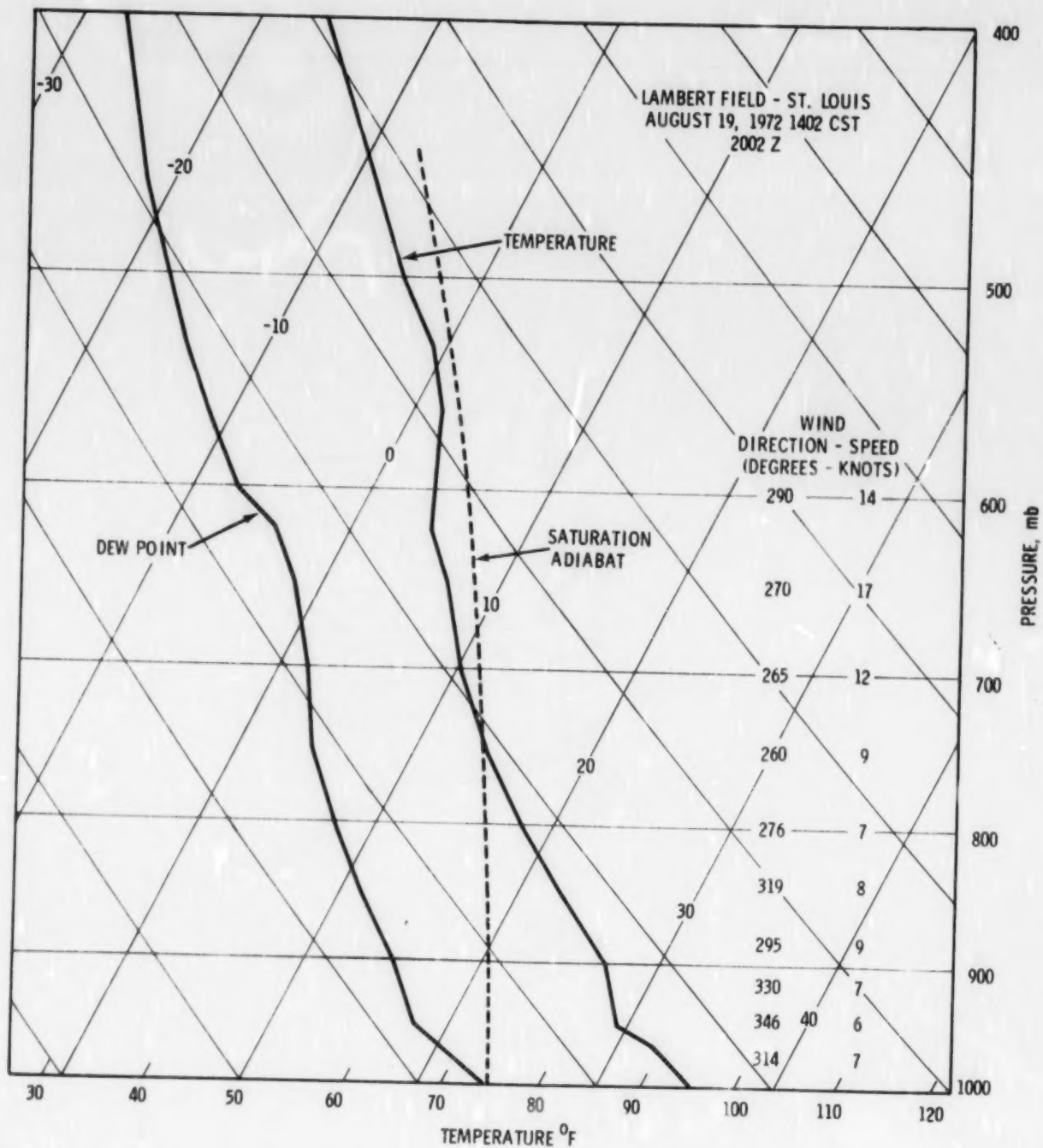


FIGURE 13. RADIOSONDE RESULTS, 1402 CST, AUGUST 19, 1972.

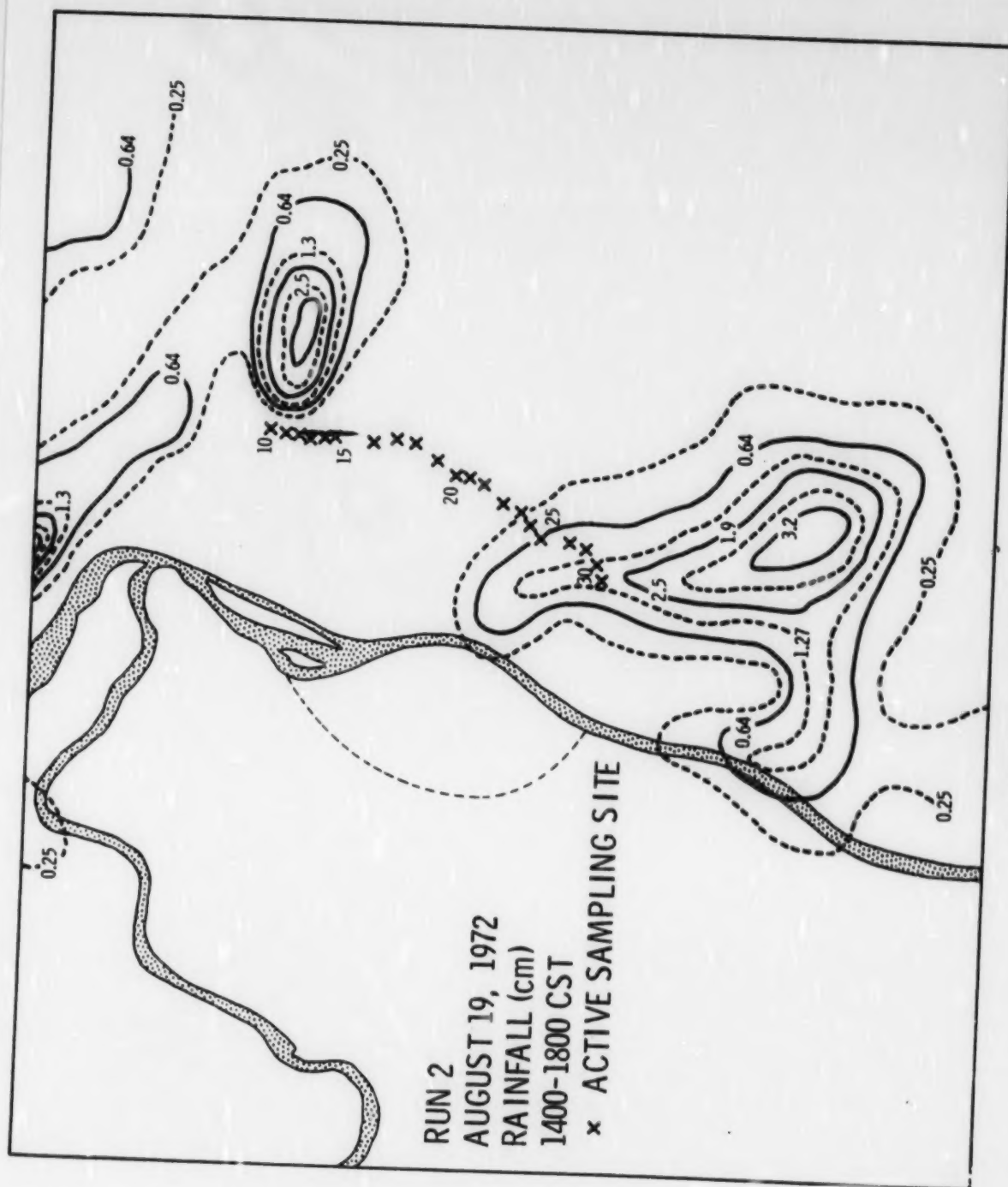


FIGURE 14. RAINFALL MAP, RUN 2.

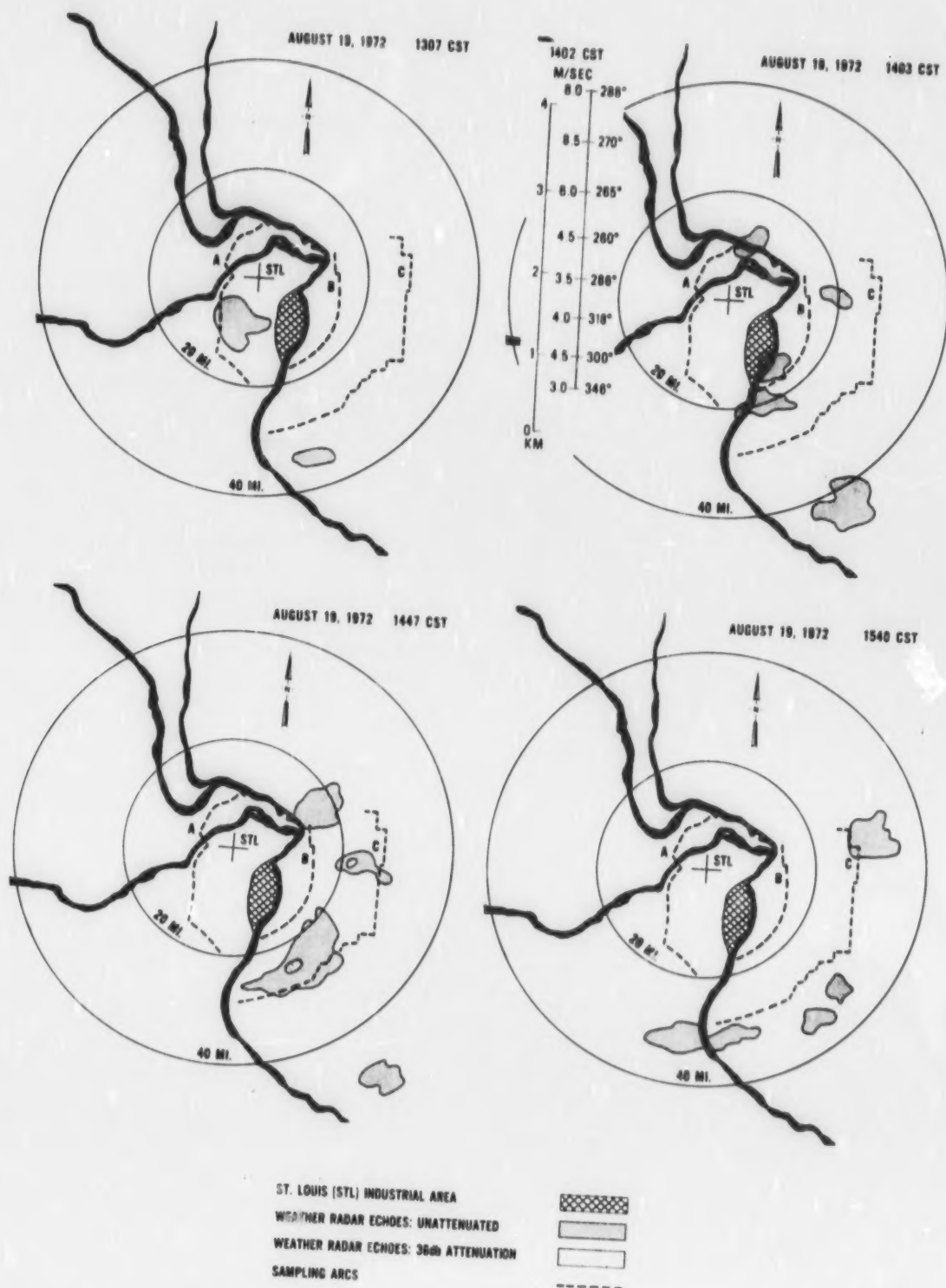


FIGURE 15. NATIONAL WEATHER SERVICE RADAR ECHO MAPS, RUN 2.

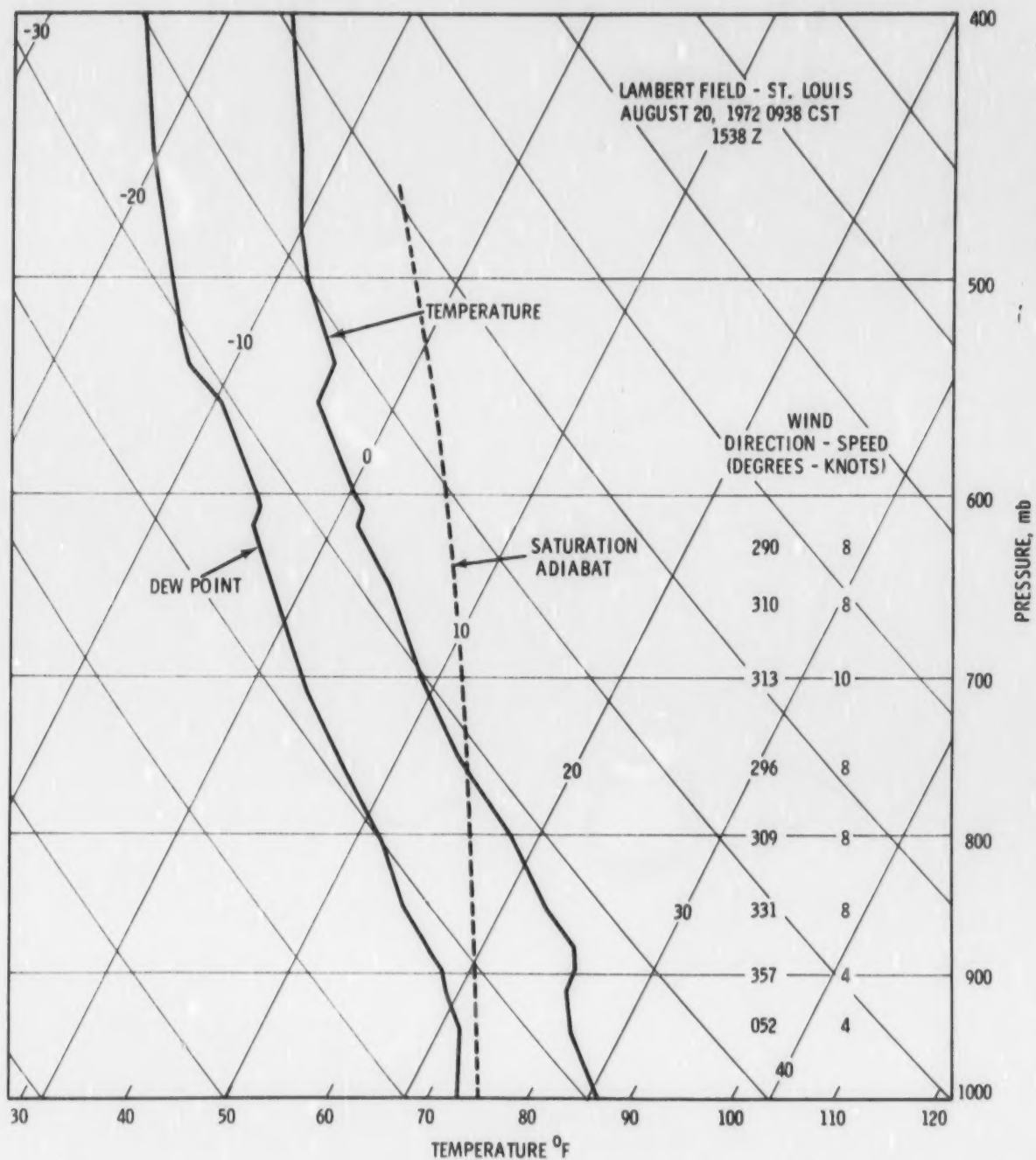


FIGURE 16. RADIOSONDE RESULTS, 0938 CST, AUGUST 20, 1972.

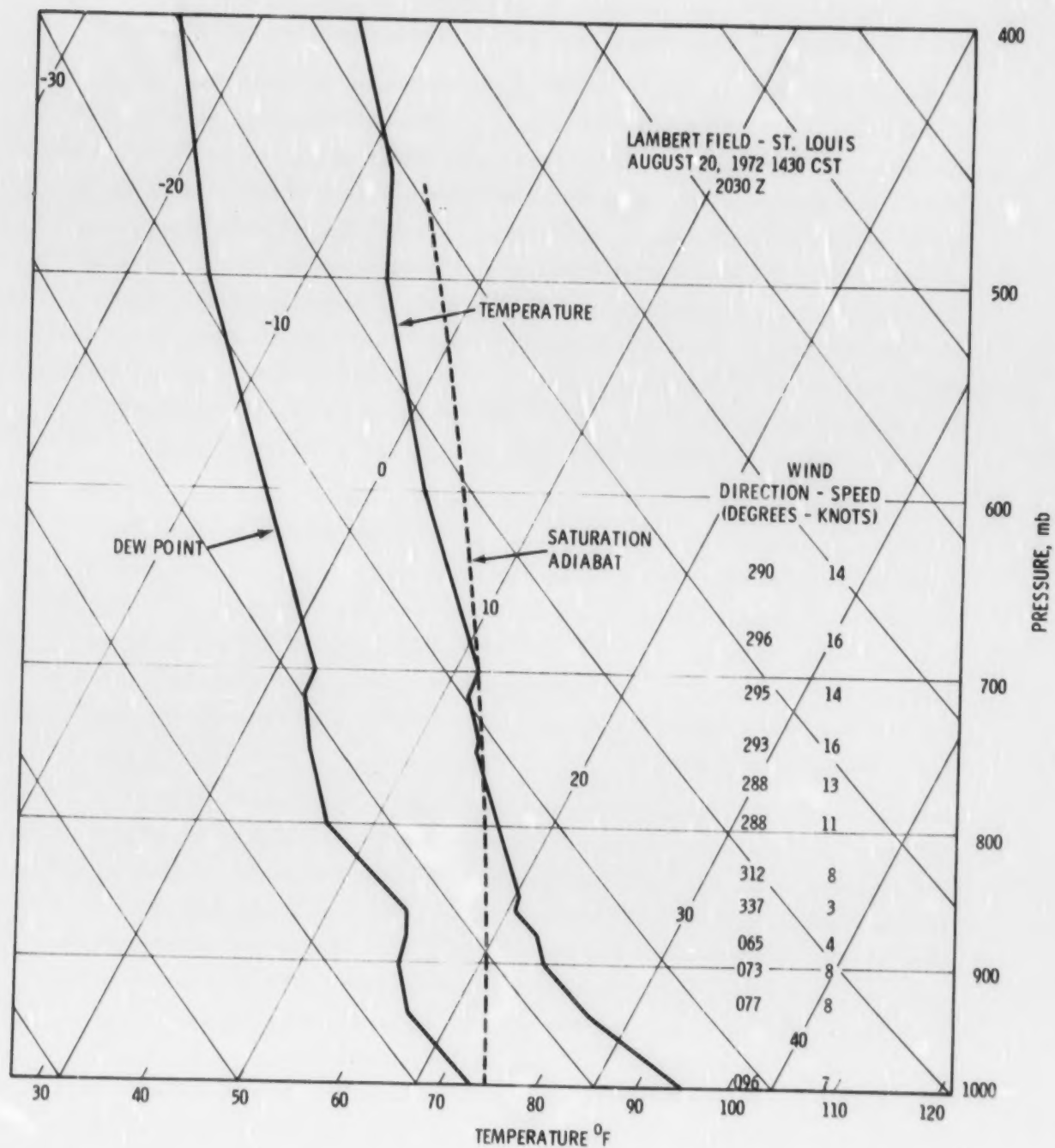


FIGURE 17. RADIOSONDE RESULTS, 1430 CST, AUGUST 20, 1972.

indicated a decrease in moisture at all levels in the interval with the earlier sounding fairly moist, and both soundings conditionally unstable.

A few cells were observed on radar to the northeast at 0940, but they soon dissipated. By 1240, a north-northwest/south-southeast line of cells had formed about 55 km east of STL. Subsequent radar observations showed rapid growth and merging of these cells as well as similar activity in an amorphous grouping 140 km west of the city. At 1540, the city was surrounded by this activity with several cumulonimbus tops reaching 15 km. Movement was minimal and disorganized, but in general the growth process brought them nearer to STL from both east and west by 1540. At 1640 the two masses had joined south of STL with a pattern of major cells in a rough east-west line with no activity to the north. No precipitation fell at Lambert Field, it being just north of the vertex of the converging cells.

A decision as to which portions of the sampling lines to outfit with collectors was hindered by an uncertainty as to which direction of storm movement would affect the St. Louis area. Finally, the northern portions of (normally upstorm) Lines B and C, and the southern portion of Line A were set out. Most of the rain at Line B fell north of the established line, and no containment was achieved there. Cells also crossed A and C, but the rain map, Figure 18, shows that the three line collections came from three distinct showers.

The rain which fell on Lines B and C came from a north-south line of activity that radar observations indicated moved very slowly if at all. The northern cell, the most intense rain of which was north of Line A, was moving about 5 km/hr from 90 degrees. The Line C cell probably did not move at all, and developed and matured in place. Any possible movement of this cell would have probably been 90 degrees also. The cell which affected Line A was apparently part of the western edge of the "V" formation of cells, and may represent an entirely different air mass. It moved from 350 degrees at about 13 km/hr, and probably originated some distance west of the city. Thus all the Run 3 collected rain came from storms whose origin and movement were not clearly related to the city's pollutant source.

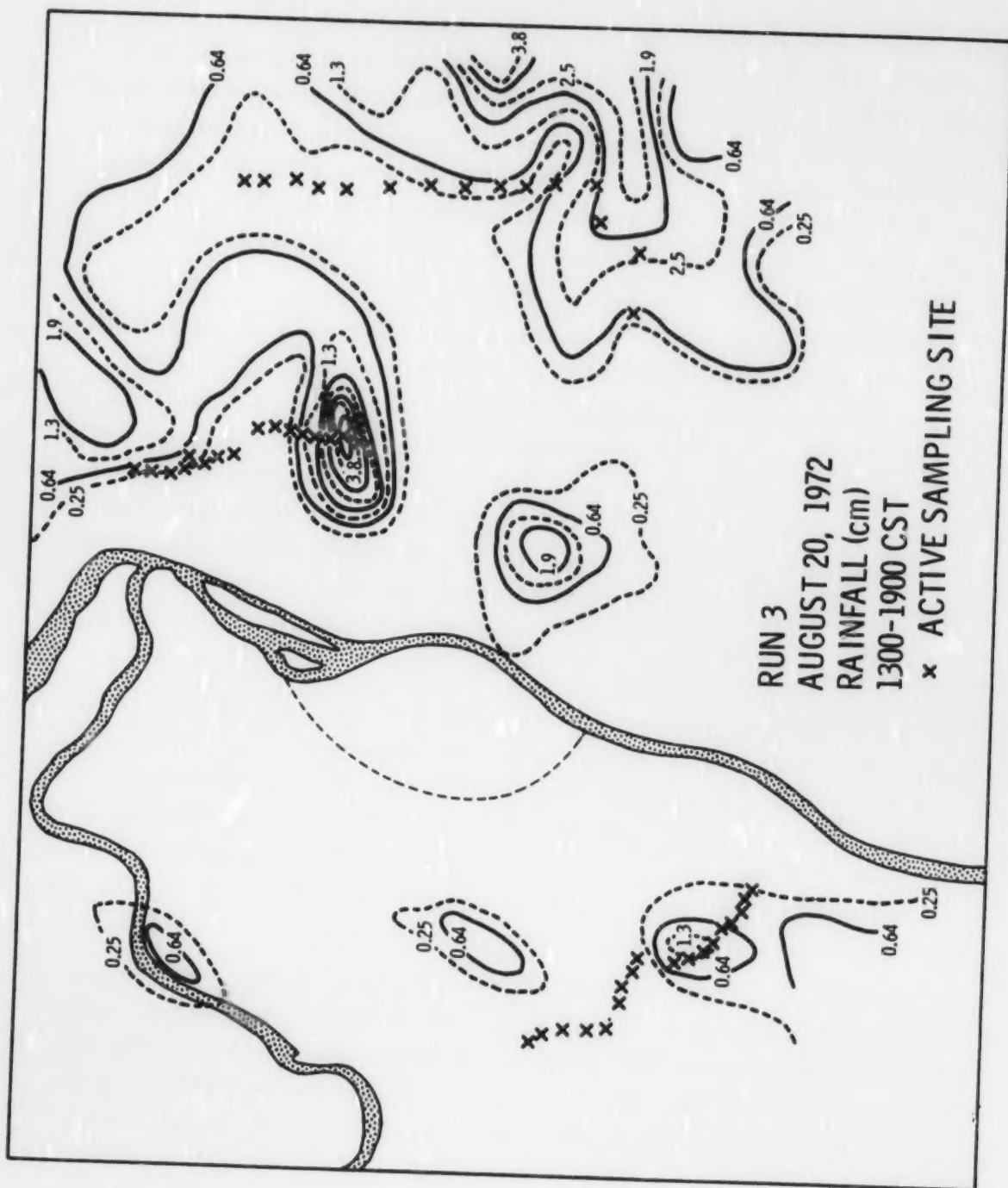


FIGURE 18. RAINFALL MAP, RUN 3.

RUN 4 (AUGUST 21, 1972)

The early morning surface weather charts showed a cold front extending from Lake Superior southwest to the Oklahoma panhandle. A squall line some 185 km in advance of the front arced from south central Wisconsin to the Kansas City area. Radiosondes were flown from the St. Louis Arch--on the downtown waterfront--at 0625 and 1130 to 700 mb, and a 1417 sounding at STL to 400 mb. The latter sounding is shown in Figure 19. All the soundings were relatively dry except for a moist layer between 800 and 750 mb on the latter two.

At 1040 radar echoes indicated a northeast-southwest line of precipitating cells 185 km northwest of STL with motion indicated from 290 degrees at 28 km/hr. At 1440 the largest area of echoes was west to southwest of STL from 55 to 230 km. At 1500, a thunderstorm began at STL, and though cells moved over the station for the next three hours, only a trace of precipitation fell. The rainfall pattern, Figure 20, and the radar maps, Figure 21, indicate that most of the intense rain development occurred south and southwest of STL. Radar plots showed strong cells rising to more than 12 km crossing the downstorm sampling lines until at least 1700. Activity continued with less intensity until about 1900.

All three sampling lines were set out, this time at double spacing to contain a greater extent of precipitation. Several small cells affected Line A, while a large mass of storm cells crossed both downstorm lines. Intense precipitation was experienced in the area; rainfall totalled 9.5 cm in downtown St. Louis, some 10 cm in Cahokia, Illinois, and over 7 cm across Line B. Strong winds felled power lines and trees along Line B, and 2 cm diameter hail was unofficially reported at Cahokia.

An examination of the precipitation patterns indicates that two separate showers affected Line A. The northern cell--which would have been an ideal storm for our purposes, had it passed over St. Louis--was long-lived and moved steadily from 260 degrees at about 25 km/hr, passing directly over Alton, Illinois. Its origin was likely some distance west of the city. The major activity which affected Lines B and C first appeared on radar about 10 km east of STL at 1510, and moved at approximately 40 km/hr from

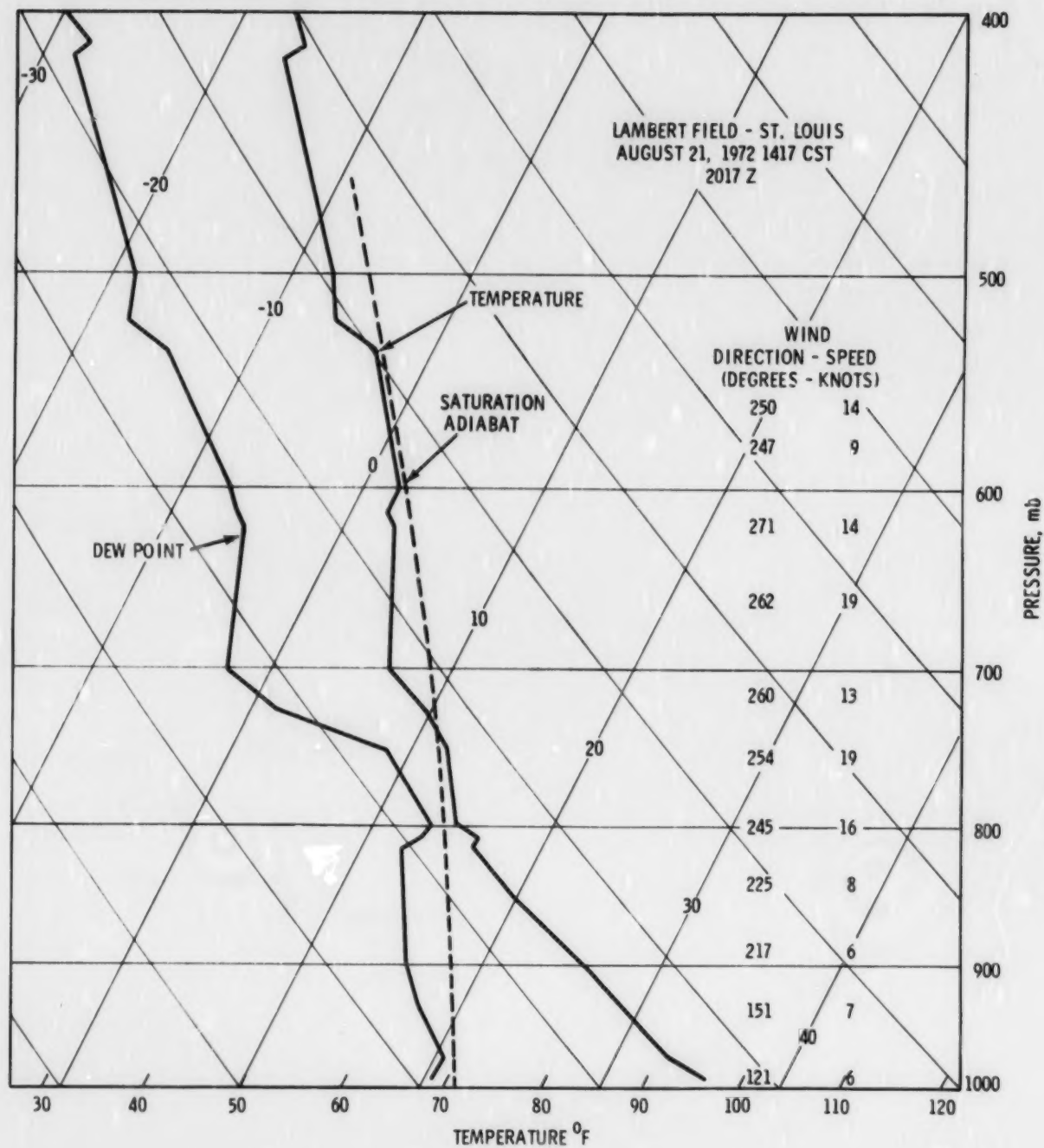


FIGURE 19. RADIOSONDE RESULTS, 1417 CST, AUGUST 21, 1972.

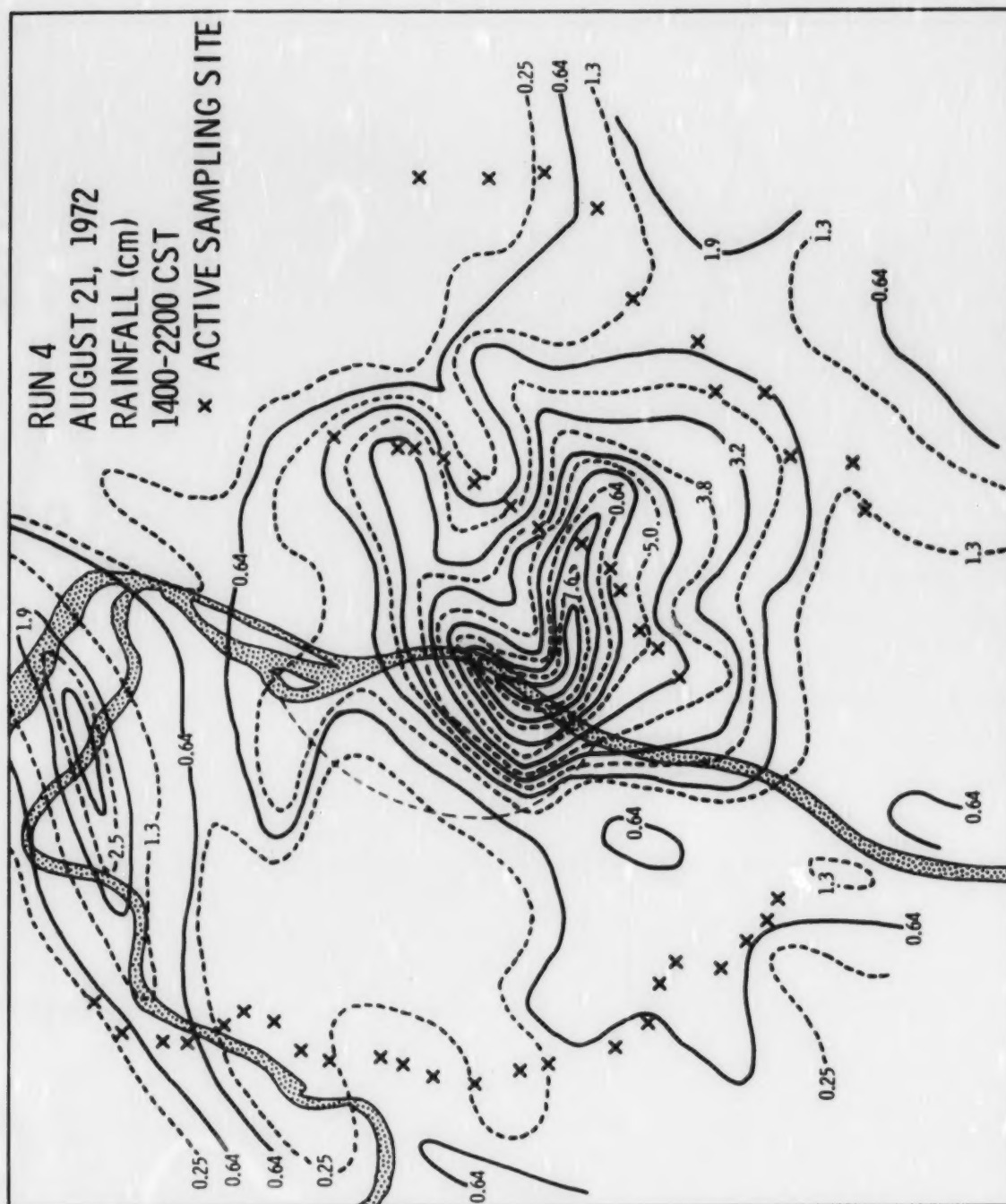


FIGURE 20. RAINFALL MAP, RUN 4.

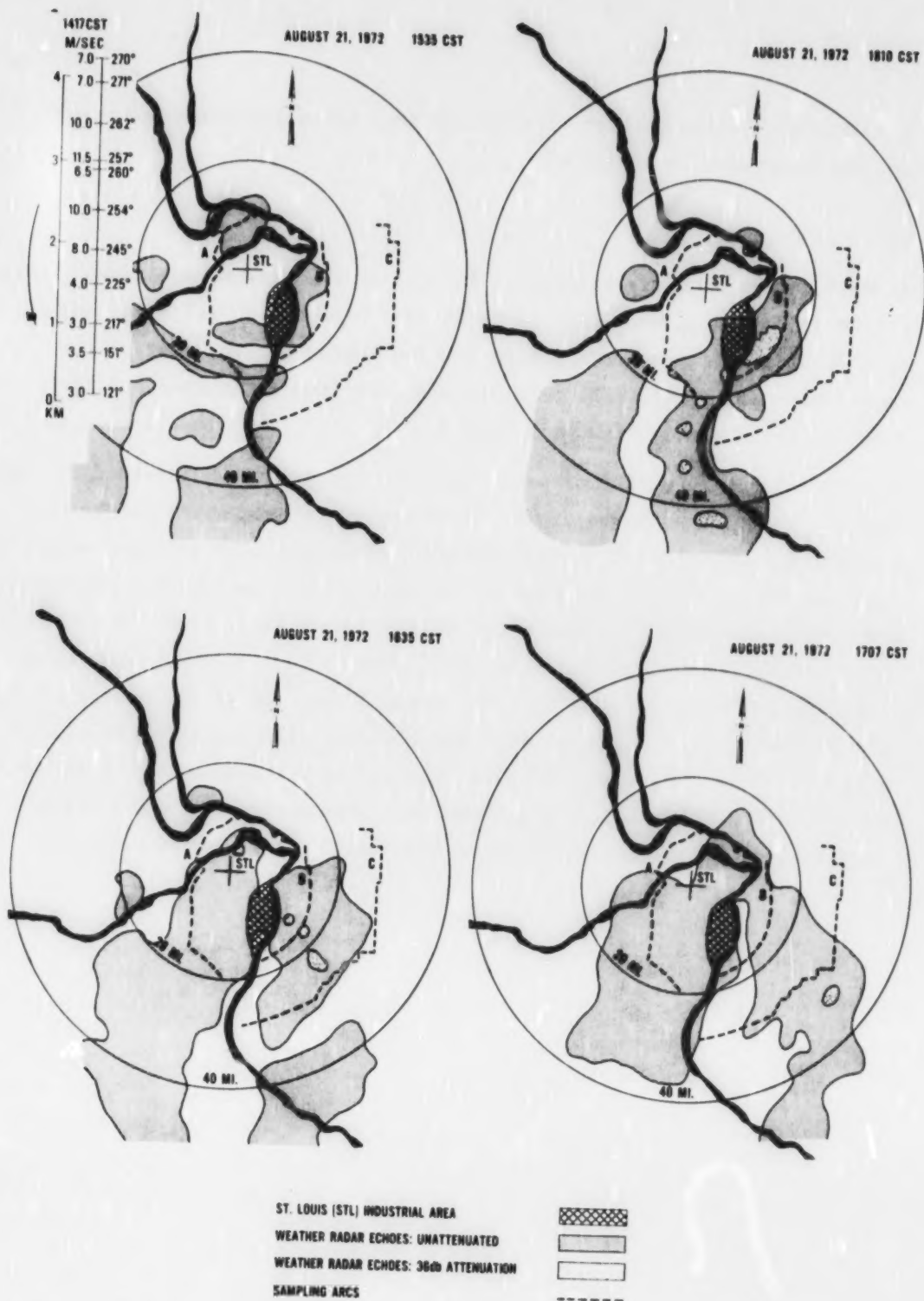


FIGURE 21. NATIONAL WEATHER SERVICE RADAR ECHO MAP, RUN 4.

320 degrees. After passing Line C, the mass of cells became more westerly, and increased in speed.

RUN 5 (AUGUST 25, 1972)

At 0600, a low pressure center was located at the Missouri-Nebraska border, a frontal wave with warm front extended to Springfield, Illinois, and a cold front extended southward from the low center to just east of the Kansas-Missouri border. Temperature profiles from radiosoundings flown from STL are shown in Figures 22 and 23.

At 0930 a 75 km-long line of cells oriented north-south approached St. Louis from 45 km to the southwest. The cloud tops were only about 7.5 km and thunder was not reported at STL, though showers began at 1035 and persisted about an hour. The line preserved its identity for two hours as it moved eastward, but numerous holes in the line appeared after 1130. A second group of cells northwest of STL at 1130 grew to form another north-south line over 500 km in length, with St. Louis 35 km east of the center of the line at 1430. This line also had gaps, however, and one group of cells passed over the city at about 1530. This group dissipated before it reached the downstorm sampling lines; thus only Line A received significant precipitation. Detailed analyses of Run 5 will not be presented here.

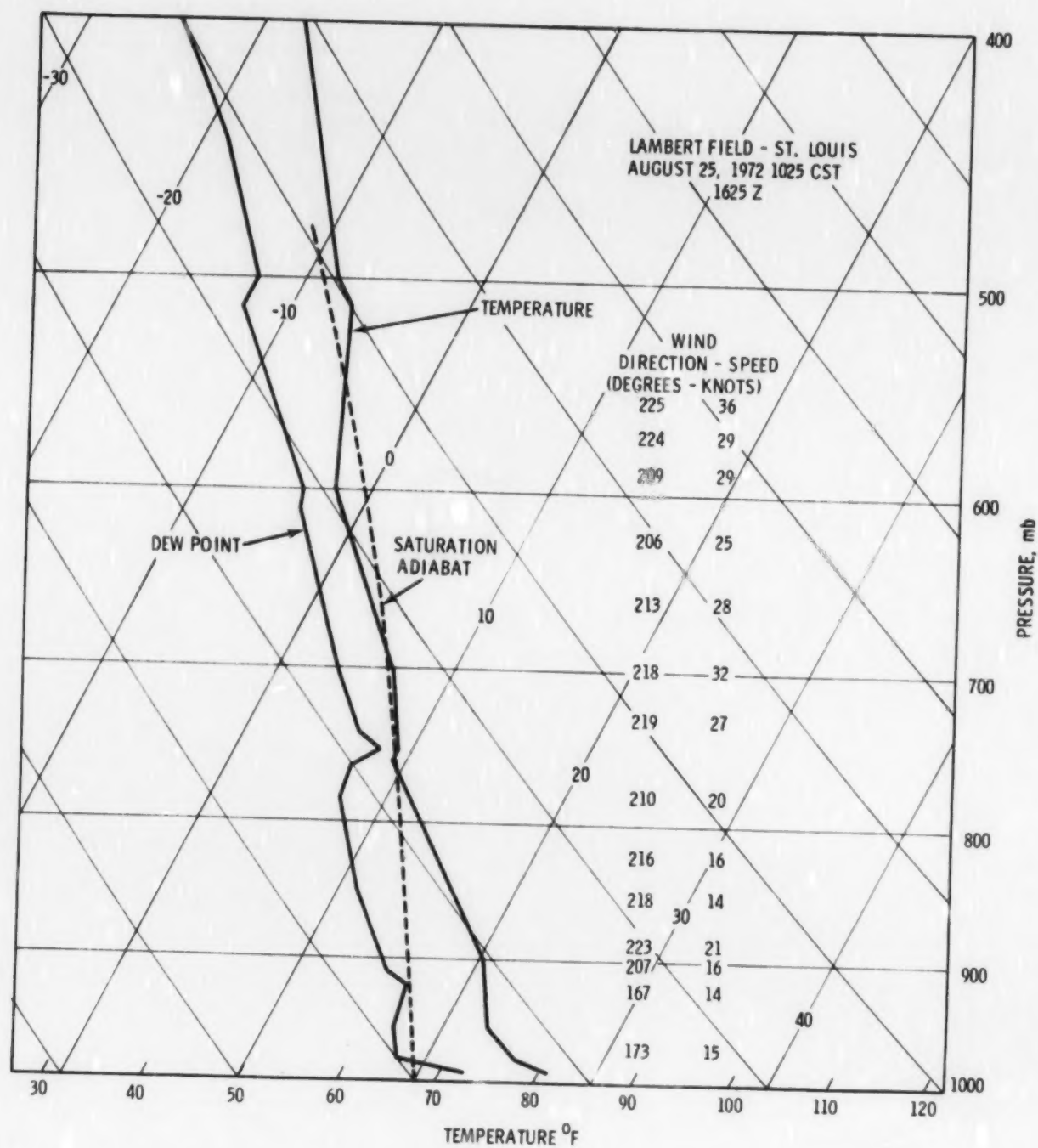


FIGURE 22. RADIOSONDE RESULTS, 1025 CST, AUGUST 25, 1972.

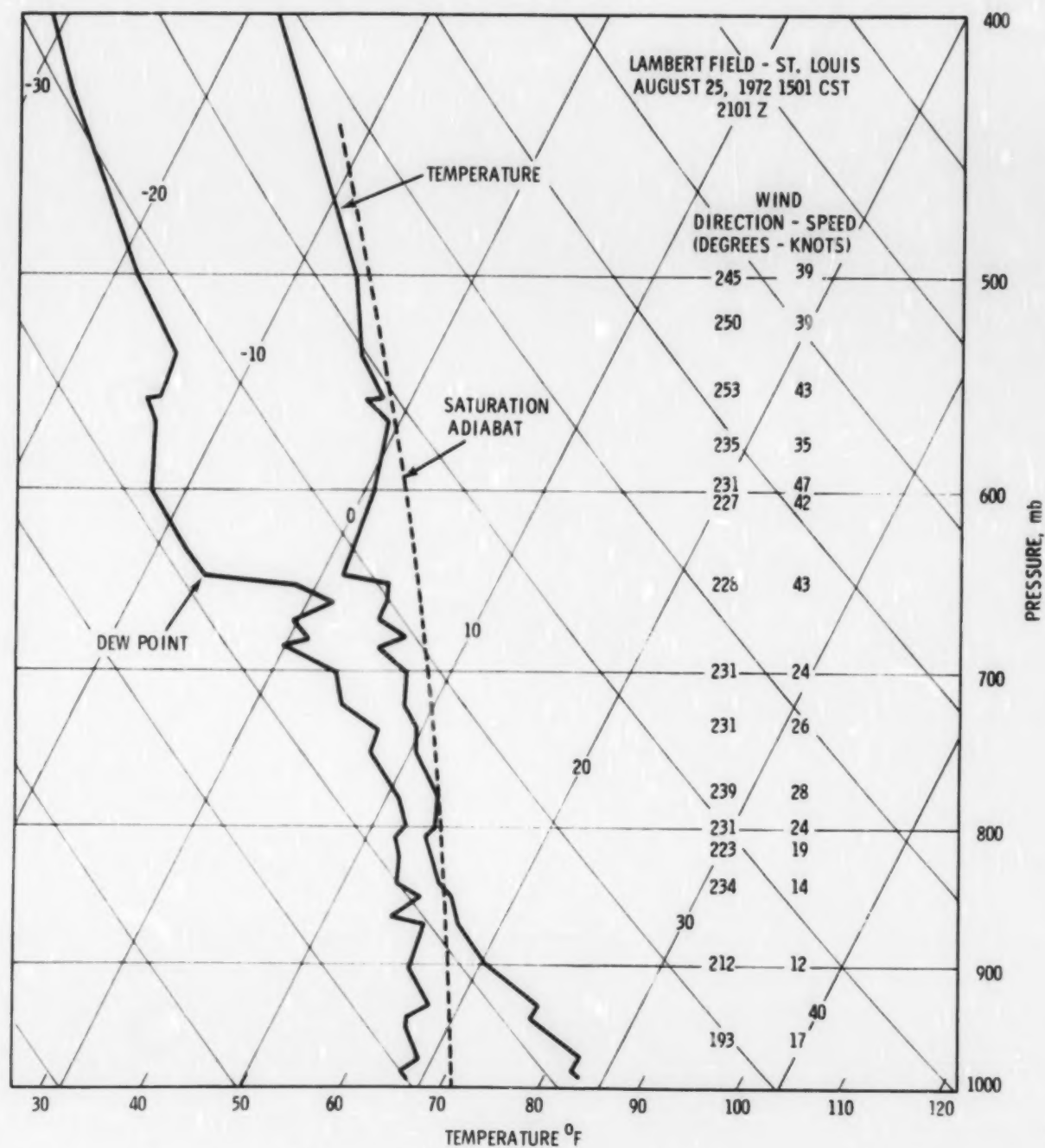


FIGURE 23. RADIOSONDE RESULTS, 1501 CST, AUGUST 25, 1972.

AIRCRAFT MEASUREMENTS

During the field-experiment period in August, 1972, several aircraft flights collected pollutant air concentrations at upwind locations, over the city, and at downwind locations at various levels in the lowest 1.5 km of the atmosphere. Though it was intended to gather this information on storm days, specifically to provide estimates of pollutant emissions for inclusion in Equation (14), scheduling difficulties allowed flights only on other days, generally in fair-weather conditions. The results of one such flight will be described here, however, to note the type and capabilities of the instrumentation involved.

On August 16, 1972, an aircraft sounding was made on tracks flown roughly perpendicular to the mean wind direction in the lowest 1.5 km. Instrumentation included a Sign-X SO₂ monitor and a condensation nucleus counter. The results for a track approximately 35 km downwind of the city at three separate levels are shown in Figure 24. Plotted is the combined concentration of SO₂ and CO₂ in parts per million (ppm). An air pollution station in East St. Louis, Illinois, operated by the Illinois State Environmental Protection Agency measured SO₂ concentrations of 0.04-0.05 ppm during the hours of the flight.

The region of enhanced concentration which is present at all three levels is probably indicative of a localized source in the Alton, Illinois area. The concentration appears to increase with height; the high concentration at about 1100 m is consistent with the presence of a stable layer at 700-1100 m upwind and over the city, and at slightly higher levels downwind of the city. The stability would act to dampen any turbulent or convective mixing between the low levels and levels above the stable layer.

The higher concentration of SO₂ at about 1100 m on the downwind pass is also consistent with the concentrations of condensation nuclei found on this flight. A portion of this data is listed in Table 6. The condensation nucleus concentration increases drastically downwind from the city at 1100 m elevation where the inversion is somewhat higher.

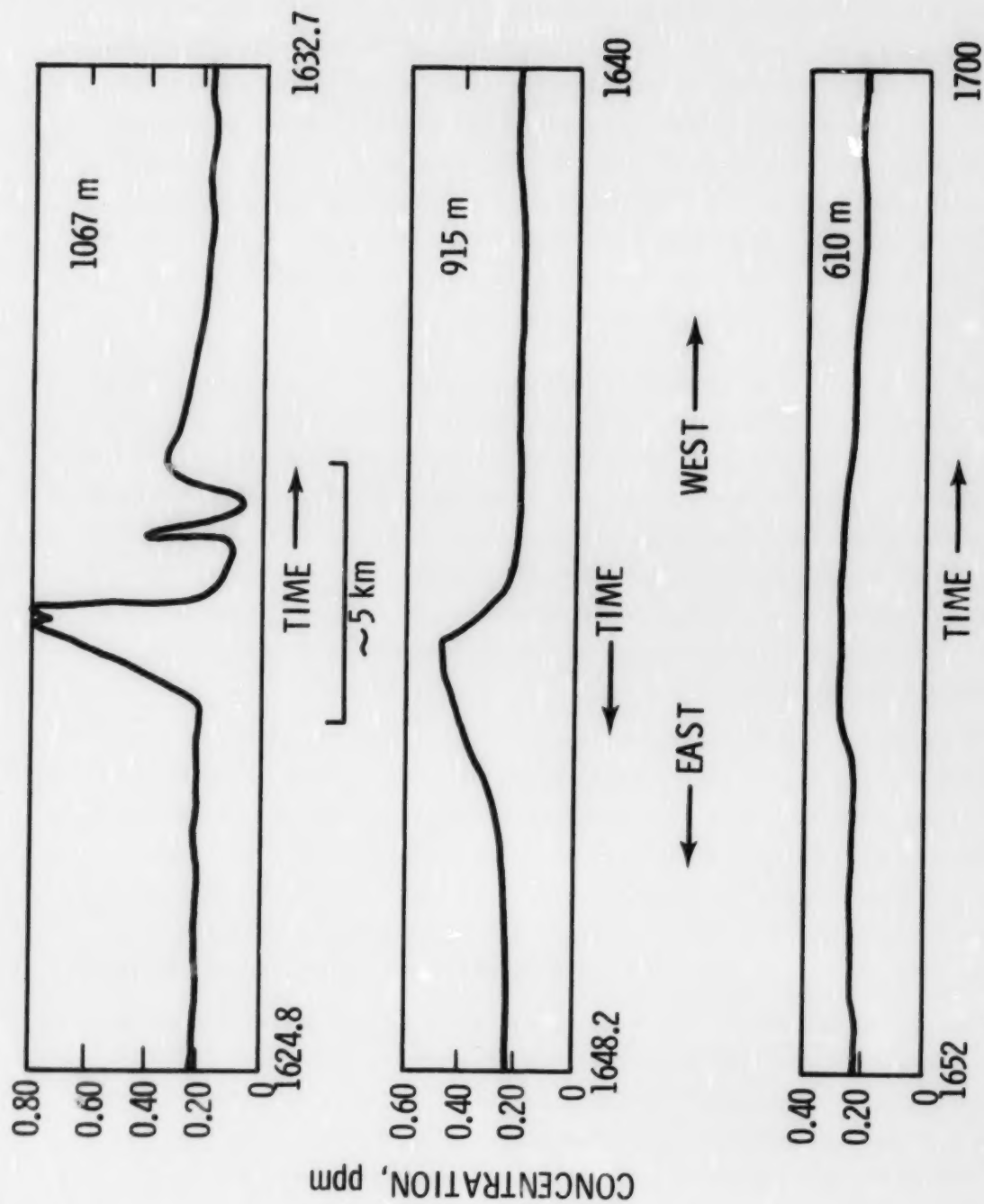


FIGURE 24. AIRCRAFT SOUNDING RESULTS FOR SO_2 AIR CONCENTRATIONS, AUGUST 16, 1972.

Table 6. CONDENSATION NUCLEI: AUGUST 16 AIRCRAFT SOUNDING.

Location of Flight Track	Condensation Nuclei Concentration in Air (cm^{-3}) $\times 10^{-4}$		
	600 m	900 m	1100 m
Upwind of City	1.9	5.0	0.11
Over City	5.0	5.0	0.14
Downwind of City	4.0	4.1	6.0

SECTION VII.

ANALYSIS OF RESULTS

The various alternative approaches to modeling precipitation scavenging in the urban environment were described in Sections IV and V. We have chosen to couch the results of this initial phase of the study in terms of evaluation of scavenging fluxes and rates which would form the scavenging input to a more comprehensive material balance model for the RAPS. The analysis of the August 1972 results necessarily must be confined in a quantitative sense to calculation of those entities as they were observed for particular convective storms. Beyond that, we hope to show the extent to which development of the various modeling approaches are possible and useful; current and future convective storm data will be of importance in validating and testing these approaches.

CHEMICAL ANALYSIS

The results of chemical analyses of the precipitation samples are listed in Table 5. Gaps in the data indicate either lost or spoiled samples or insufficient rain volume available for analysis. Each analysis required a separate volume of water; about 50 ml or 0.15 cm of rain was required to perform all six analyses. The only unsatisfactory overall analysis run was that for nitrate for Run 1. The sensitivity was very poor; concentrations that were apparently very high were judged too doubtful for reporting due to uncertainty in the calibration.

Some of the later run samples were returned to Richland, Washington, for repeat analyses for nitrate and NH_4^+ ; the chromotropic acid analysis, an independent means of determining nitrate content, was also performed on several samples. Good agreement was observed between the two methods of nitrate analysis on the average, but there was a scatter of about $\pm 15\%$ on individual samples. The second analysis for ammonium ion, which took place after several stages of thawing and freezing for prior analyses, showed systematically higher readings than the first analysis. Some

recent work, which will be described in a later report, indicates that with aging and handling there appears to be an increase in apparent ammonium content. In view of these developments, which are still under study, we are placing greater value on the first measurements, which are those listed in Table 5.

AVERAGE RAINWATER CONCENTRATIONS

The average pollutant concentrations for each sample line are listed in Table 7. These can give some insight into relative rainwater content at various distances from the city both up- and downstorm, but the upstorm values--particularly 4A and 5A--do not necessarily represent background concentrations. Though the general storm motion was west to east in these runs, the low-level air entered from the opposite direction. Thus, significant scavenging of urban pollution could have taken place over Line A. These data are certainly too limited to lead to firm conclusions, but their consistency and magnitude somewhat lower than the Line B average concentrations suggests that this low-level effect--possibly due to washout only--is smaller than the general downstorm scavenging effects. It should be noted, however, that residence times of pollution within the storms also affect relative positions of uptake of pollution and deposition on the ground. It is interesting to note here the strikingly similar concentrations on Line A and C of Run 4. The intensity of the storm as it developed from the city eastward may possibly have removed a large part of the urban pollution output before Line C. Though the rainfall on Lines A and C are not directly related in terms of continuity of rainfall across the entire area, the similar concentration values may be a result of sampling of background concentrations.

We do not report any SO_2 concentrations; no rain sample was found to have a significant amount of SO_2 present. These results are not surprising, inasmuch as the solubility of SO_2 in water is greatly reduced when the concentration of hydrogen ions is high.¹⁴ The acidity of the St. Louis area rain was found to be uniformly high, as the tables show. It would be expected, however, that significant concentrations of SO_2 would be found

Table 7. SAMPLING LINE AVERAGE CONCENTRATIONS:
AUGUST, 1972.

Run/Line	Concentration ^a (gm-moles/l) x 10 ⁶				
	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
1/B	40.1	0.16	b	17.1	114.
2/B	171.	0.42	121.	33.0	87.5
3/C	144.	0.21	51.4	30.8	125.
3/B	172.	0.10	169.	66.3	170.
3/A	176.	0.13	156.	52.9	181.
4/A	59.4	0.28	54.2	19.4	42.6
4/B	98.2	0.44	72.1	23.9	46.7
4/C	63.2	0.12	61.2	19.4	44.7
5/A	59.9	0.09	c	c	c

^a All SO₂ concentrations were insignificant.

^b Analysis unsatisfactory.

^c Insufficient water for chemical analysis.

in rain sampled near local strong sources, despite the high overall acidity; apparently all the samples collected during the current study were not affected by local sources.

We must also note here that though the nitrite average data are listed in Table 7 and in subsequent analyses, the observed irregularity of the concentrations along sample lines as compared with the major species, as well as the generally very low concentrations, gives the impression that local sources (such as highway traffic) may be more important for nitrite than overall urban sources. Thus they are listed for comparison only, and should not be considered seriously as an indication of the overall urban nitrite source effect on scavenging.

SCAVENGING FLUXES AND RATES

In order to calculate the scavenging rates using Equation (15), we must first evaluate the individual scavenging fluxes. These can be derived from the measured concentrations, as the flux is just the product of the concentration and the rainfall rate $J = V/\alpha T_r$, where V is the volume of rainfall collected, α is the area of one collector and T_r is the time of rainfall at the collector site. Two complicating factors must be considered, however. First, an evaluation of T_r must be made, since the time of rainfall is not in general the same as the total collection time T_t ; i.e., there often was a period of time prior and/or subsequent to the rainfall during which the sampler was deployed. This evaluation must be done by estimation from raingage records. The second factor to consider is that the measured concentration of pollutant was actually the total concentration resulting from both dry and wet deposition processes. In fact, the total flux F is

$$F = d + w, \quad (16)$$

where d and w refer to dry and wet, respectively. In terms of measured quantities, this is

$$C_t V/\alpha T_t = d + C_r V/\alpha T_r. \quad (17)$$

We made no measurement of d during this study, but if it can be ascertained somehow that d was small compared to w , then it would be assumed that $C_r = C_t$, and the rain flux can be calculated with T_r provided by an examination of raingage records.

Estimate of Dry Deposition Flux

The dry flux d is often defined as the product of the air concentration χ (at the ground surface or some reference level) and a deposition velocity v_d , which is ostensibly a function of the particle size and chemical and physical properties of the pollutant. Any significant vertical motion of

the air near the ground should also affect the value of v_d . We measured neither χ nor v_d directly during this study, but reasonable estimates may be made of them which will aid in evaluating any dry deposition impact on our concentration data. Table 8 lists selected urban and nonurban air concentrations as reported by the National Air Surveillance Networks for 1968.¹⁵ There were no data reported for urban St. Louis, but East St. Louis, Illinois, is included, which may be more relevant to our downstorm measurements. Also in Table 8 is an estimate of deposition of material of the listed air concentration, if the deposition velocity $v_d = 5$ cm/sec. This value is conservatively high, being equivalent to the settling velocity of a particle of radius 20 microns.¹⁶

Scavenging Fluxes

The observed total flux values for our samples were in general much higher than the rough estimates for dry deposition in Table 8. Thus, for the purposes of calculating the rain fluxes and scavenging rates for the sample lines, it was assumed that $C_r = C_t$. Figures 25 to 29 show the rain scavenging fluxes plotted as a function of sample position (y coordinate) along the sample lines. The sampling positions are located on Figure 9. Hourly data from the Illinois State Water Survey rain gage network were used to estimate T_r , the time of rainfall. These estimates were aided by our field notes concerning rainfall start and stop times. On runs when the total sampling and rainfall times were fairly short, errors of up to $\pm 50\%$ are possible in the flux data, as the raingage data reported only the amounts within a given hour. The total sampling times were kept as short as possible, however, so that T_r averaged about 75% of T_t . It is therefore advisable to consider the flux data of Figures 25 to 29 as only for comparison, rather than as exact expressions of the rain flux. In subsequent calculation of the scavenging rates, involving summation over the sample line, the errors tend to cancel somewhat. Most of the rainfall volumes used in calculating the fluxes are those which we measured in our collectors. These amounts agreed reasonably well with amounts interpolated from our maps made from the Illinois State Water Survey precipitation data (Figures 11, 14, 18, and 20). The raingage data were used, however, to fill in missing sampler amounts on Run 4, Line B.

Table 8. SELECTED AIR CONCENTRATIONS OF PARTICULATE POLLUTANTS FOR MIDWEST CITIES, AND ESTIMATED MAXIMUM DRY DEPOSITION FLUX FOR $v_d = 5$ CM/SEC.

Site	Air Concentration (gm-moles/m ³) $\times 10^6$						Estimated Average Dry Deposition Flux ($v_d = 5$ cm/sec) (gm-moles/cm ² sec) $\times 10^{12}$		
	SO ₄ ⁼		NO ₃ ⁻		NH ₄ ⁺		SO ₄ ⁼	NO ₃ ⁻	NH ₄ ⁺
	Avg.	Peak	Avg.	Peak	Avg.	Peak			
<u>Urban</u>									
E. St. Louis, Il.	11.2	19.0	2.2	4.3	0.7	3.3	0.6	0.2	0.2
Louisville, Ky.	16.0	31.0	3.8	8.6	0.4	2.7	0.8	0.3	0.1
Nashville, Tn.	9.5	23.0	2.9	5.5			0.5	0.2	
Memphis, Tn.	5.6	13.4	2.8	5.1	0.2	1.3	0.3	0.2	0.1
Kansas City, Mo.	6.2	18.0	2.7	6.3	0.1	0.8	0.3	0.2	0.03
<u>Nonurban</u>									
Shannon Cty., Mo.	4.7	10.4	1.1	2.5	0.2	1.5	0.2	0.1	0.1
Parke Cty., In.	6.9	15.2	0.7	3.1	0.2	1.4	0.4	0.1	0.1
Monroe Cty., In.	9.7	27.5	1.2	3.4	0.5	3.6	0.5	0.1	0.1
Thomas Cty., Nb.	1.7	5.0	0.4	1.2	0.1	0.1	0.1	0.03	0.03

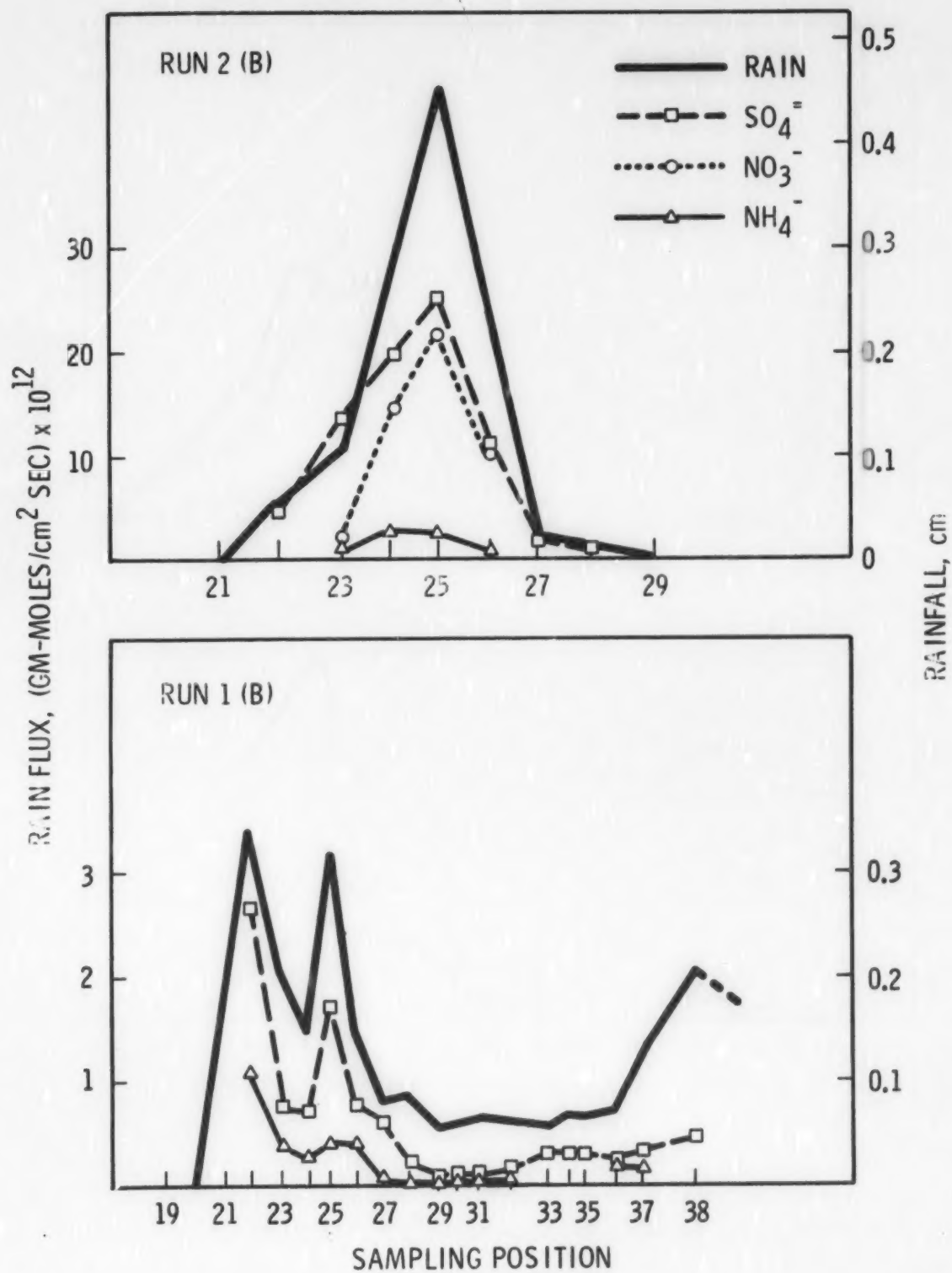


FIGURE 25. RAINFALL AND RAIN POLLUTION FLUXES, RUNS 1 AND 2.

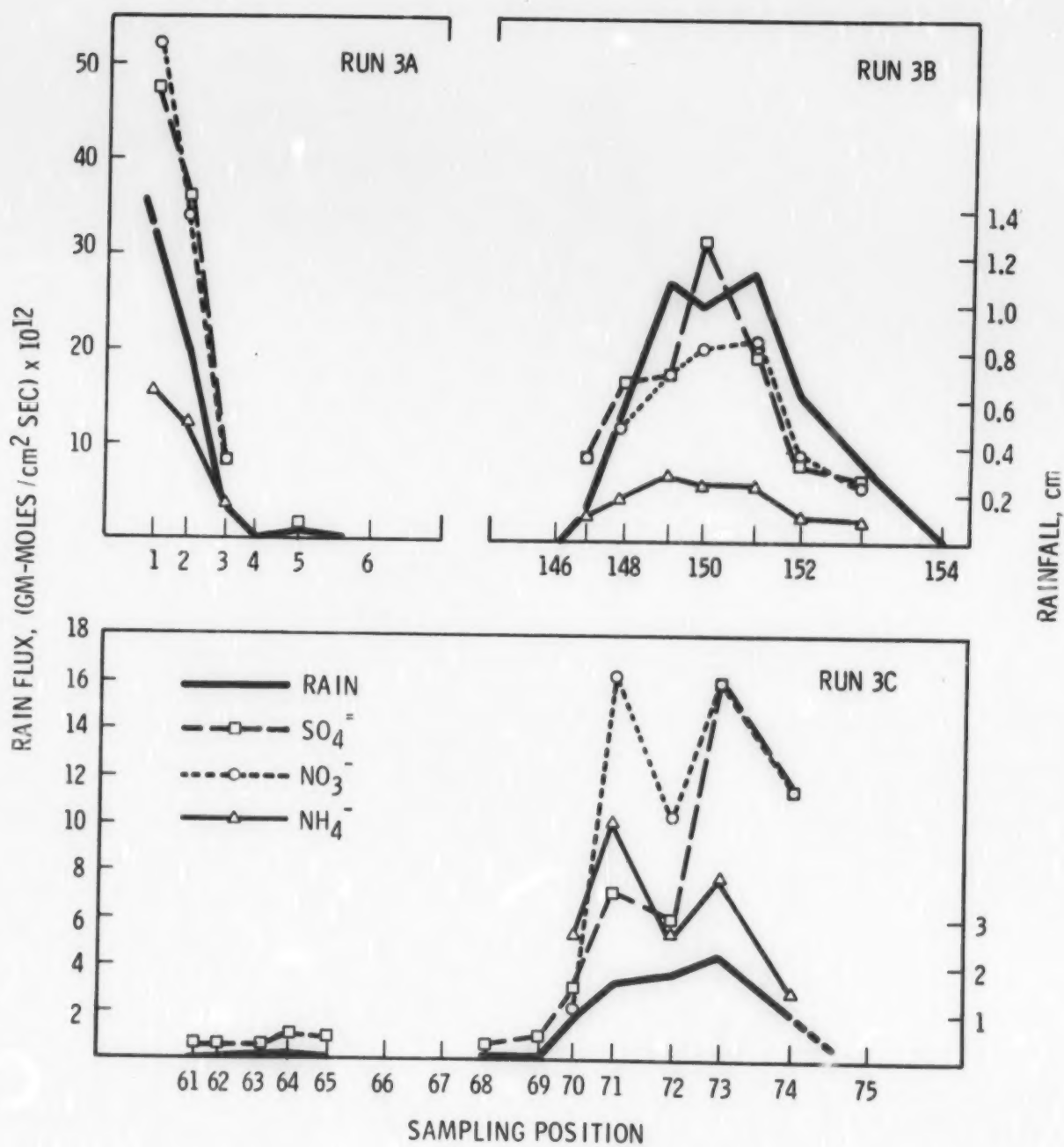


FIGURE 26. RAINFALL AND RAIN POLLUTION FLUXES, RUN 3.

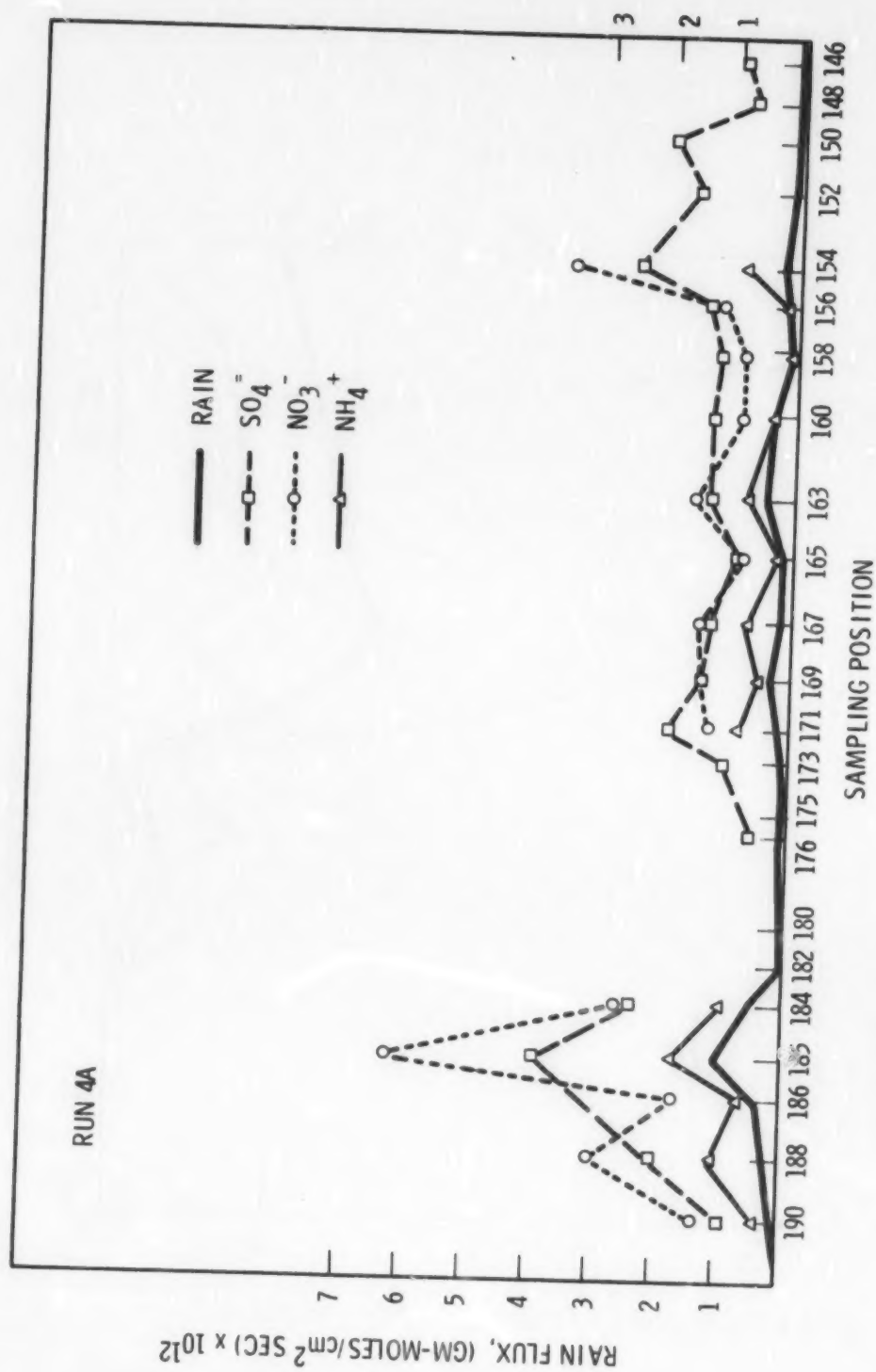


FIGURE 27. RAINFALL AND RAIN POLLUTION FLUXES, RUN 4, LINE A.

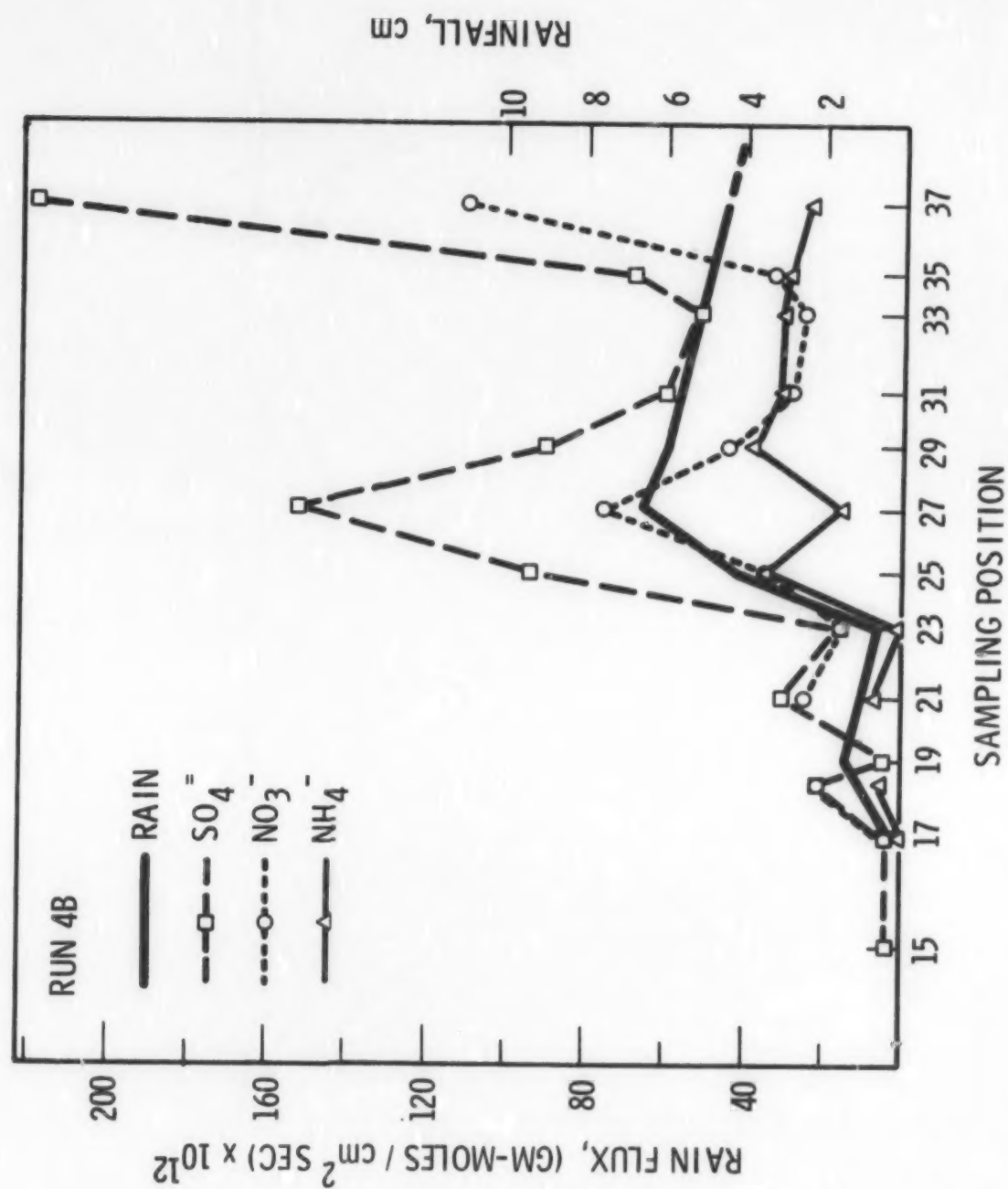


FIGURE 28. RAINFALL AND RAIN POLLUTION FLUXES, RUN 4, LINE B.

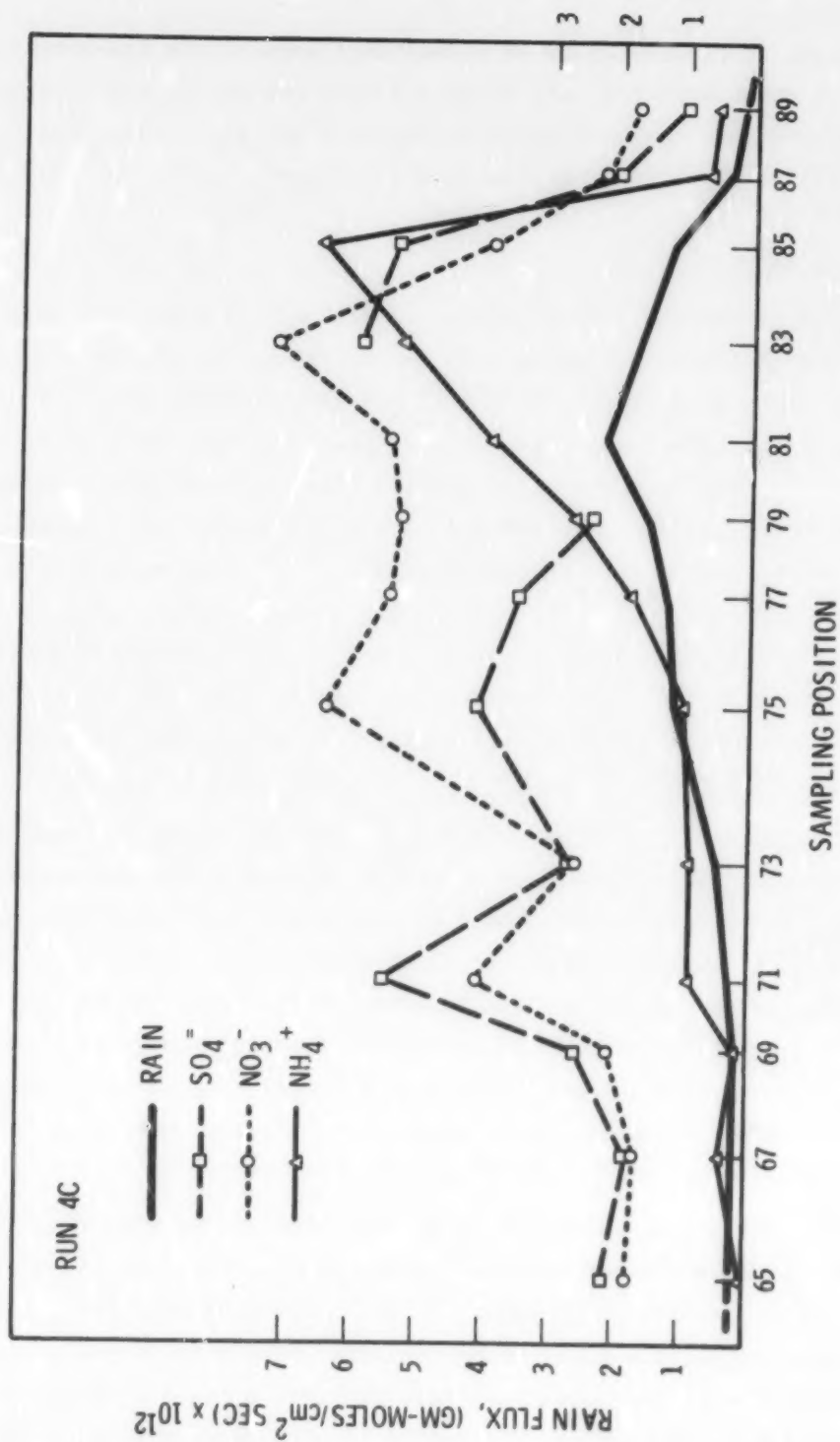


FIGURE 29. RAINFALL AND RAIN POLLUTION FLUXES, RUN 4, LINE C.

Examinations of Figures 25 to 29 reveal that some of the low-rain samples had fluxes which were not large compared with the dry flux estimates made above. These then may be considered doubtful as rain fluxes, due to the possibility of significant dry deposition present.

Scavenging Rates

As we noted in Section V, containment of the rainfall, but not necessarily containment of the city's plume, was considered a requirement for calculation of scavenging rates. We should caution, however, that the calculated rates for individual lines only reflect the scavenging conditions which apply to the locale of the sampling line. For example, the Run 2 rain collection, because of timing of setout, contained the rainfall of a portion of the main shower, slightly to the side of the main shower, and trailing it in time. Thus the source of pollution contributing to the scavenging rate is generally in doubt; in most cases, it is expected that only a portion of the city's output is involved, plus possibly a contribution from washout of low-level air moving from a direction different from that of the motion of the storm.

The scavenging rates, calculated from Equation (15) using the rain flux data, are shown in Table 9. Run 3, Line B, and Run 5 are not included because of insufficient containment of the rainfall. In the case of Run 4, Line A, the gap in the rainfall required that the two portions be separated for scavenging rate purposes, but it is noteworthy that the two apparently different showers (cf. Figure 20) resulted in roughly the same scavenging rates. As noted above, the nitrite data possibly reflect local source contributions more than the other species, so nitrite scavenging rates are included only for a rough comparison with the others.

In relating scavenging rates for different lines of the same run, it is true that the relationship will not be the same as that for the average concentrations, as listed in Table 7. The scavenging rate results essentially from the average flux, which includes the effect of rainfall rate. For example, the 4C concentrations were similar to the 4A concentrations, but the rainfall rate was much higher on Line C, leading to a higher scavenging rate.

Table 9. SCAVENGING RATES: AUGUST, 1972.

Run/Line	SO ₄ ⁼	Scavenging Rate (gm-moles/cm sec) x 10 ⁶		
		NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺
1/B	0.92	0.002	a	0.32
2/B	6.62	0.014	6.60	1.84
3/C	10.3	0.009	11.5	6.52
3/A ^b	8.49	0.006	7.33	2.49
4/A (North)	2.21	0.028	2.92	0.97
4/A (South)	3.83	0.004	3.55	1.37
4/B	192.	0.516	128.	55.4
4/C	18.0	0.024	22.1	10.9

^aNo measurement.

^bRain not sufficiently contained on 3/B.

In general, the scavenging rates, which express the rate of removal of pollution in terms of mass per unit time per unit distance, do not give much insight into more absolute rates of removal which reflect the magnitude of the pollution source. But with Run 4, we have independent measure of scavenging rates for two distances downstorm. These data allow very crude integration of the removal over the x direction. If we assume that there is no further source of pollution to the storm between Lines B and C, i.e., that the airborne pollution at Line B can only decrease by scavenging as it moves downstorm, the fractional removal is

$$F_{BC} = \frac{W(\text{line B}) - W(\text{line C})}{W(\text{line B})} \quad (18)$$

A more useful calculation, but equally crude, involves carrying the integration of the last term of Equation (14) one more step to include the x direction. We have calculated

$$W = \int_0^b w(x, y) \partial y = \sum_{i=1}^{n-1} \frac{(w_i + w_{i+1}) |y_i - y_{i+1}|}{2} \text{ (moles/cm sec).} \quad (15)$$

The next step, which for Run 4 involves just a two-step approximation to the integration, is

$$\Omega = \int_{x_B}^{x_C} W(x) \partial x \cong \frac{W(x_B) + W(x_C)}{2} [x_B - x_C] \text{ (moles/sec),} \quad (19)$$

where x_B and x_C are the distances from the St. Louis arch to Lines B and C, respectively. Table 10 lists values of F_{BC} and Ω calculated for Run 4; the latter compared with approximate 1963 emission rates for St. Louis County, and St. Clair County, Illinois (E. St. Louis).¹⁷ Clearly, the simple averages derived from consideration of only two points downstorm can only give a rough estimate of the magnitude of the scavenging effect of this particular storm, but it is noteworthy that--though the exact pollution source is unclear--the deposition in one downstorm area was comparable to the emission in the urban area.

Table 10. FRACTIONAL REMOVAL AND RATE OF REMOVAL BY SCAVENGING FOR RUN 4, LINES B AND C.

Pollutant	F_{BC}	Ω (moles/sec)	Approximate St. Louis Emission Rate - 1963 ¹⁷ (moles/sec)
$SO_4^{=}$	0.91	189.	69.
NO_3^{-}	0.83	135.	39.
NH_4^{+}	0.80	60.	a

^aNot available.

APPLICATION OF A COMPREHENSIVE STORM MODEL FOR SCAVENGING ANALYSIS

The two-dimensional convective storm model mentioned previously in Section IV has been applied for limited analyses of the 1972 field results. As noted previously, this model is essentially a solution of the transient conservation equations for mass, water vapor, liquid water, momentum, and energy, subject to appropriate constraints and boundary conditions, and is described in detail elsewhere.⁸

The approach that has been utilized thus far involves first obtaining a realistic storm cell circulation using the model in conjunction with measured environmental conditions. Steady state motion and liquid water fields are then assumed and a plume of pollutant is inserted ahead of the storm. Subsequently, three separate calculations are performed, each more complicated than the one preceding.

1. The air motions in the storm are allowed to redistribute the material, with no interaction with rain.
2. Same as 1., except that below-cloud scavenging processes are added.
3. Same as 2., except that in-cloud scavenging processes are added.

An example of the results of 1. is presented in the following pages, while 2. and 3. are included in future research plans. Since the form of the pollutant plume on the day in question was not measured by aircraft, future calculations will be performed using several initial spatial distributions of the pollutant to be scavenged. The calculated deposition patterns resulting from diverse initial conditions and processes may then be compared with the observed pattern.

TEST CASE: ENVIRONMENTAL CONDITIONS AND RESULTS OF CALCULATIONS

The squall line thunderstorm model has been applied for a test case using the environmental conditions existing in the St. Louis area on August 21, 1972, the day of Run 4. The storm which occurred on that day possessed several squall line characteristics. The rainfall pattern is shown in Figure 20 as measured by the raingage network operated by the Illinois State Water Survey. Amounts in excess of three inches were measured in southeast St. Louis and directly across the Mississippi River in Illinois.

The elongated rainfall maximum in the northern section of the area resulted from the movement of a separate cell toward the east-northeast. The rainfall pattern in the south part of the city represents the movement of individual cells in an easterly direction, but with development of new cells quasi-continuously on the right flank. The result of this was a propagation toward the southeast.

The wind, temperature, and moisture profiles were measured at approximately 1400 CST, a few hours prior to the storm's occurrence. The winds which were used in the two-dimensional model calculation were the components of the wind in the direction of storm motion (taken to be from the northwest (315°)). The resulting wind profile is shown in Fig. 30. Actually two wind profiles were used in the model calculations, one profile to the left and one profile to the right of the storm, so as to produce low level convergence and upward motion. The profile shown in Fig. 30 is actually the mean of these two profiles. The temperature, water vapor mixing ratio, pressure, and air density as shown as functions of height in 400 m increments in Table 11.

The model calculations were initiated by allowing the area of upward motion to produce a convective cloud. The evolution of the cloud is represented by the time variation of several parameters shown in Fig. 31. The model was run for about 60 minutes until a fairly regular oscillatory time evolution of the cloud circulation was obtained. A time was chosen (about 55 minutes) when a typical cloud circulation was occurring. The motion field, rainwater mixing ratio distribution and cloudwater distribution were then assumed to be fixed in time for purposes of experimentation with pollutant inclusion into the storm. The streamfunction, representing the motion field, is shown in Fig. 32. A pollutant distribution was then introduced in the lower 2 km of the atmosphere upwind from the storm. The pollutant was then allowed to travel with the air motion (motion field is that relative to the moving storm, translational speed has been removed) and not allowed to interact with the rain or cloud. The distribution was allowed to enter through the right boundary for a limited amount of time corresponding to the finite width of a pollutant over an urban area.

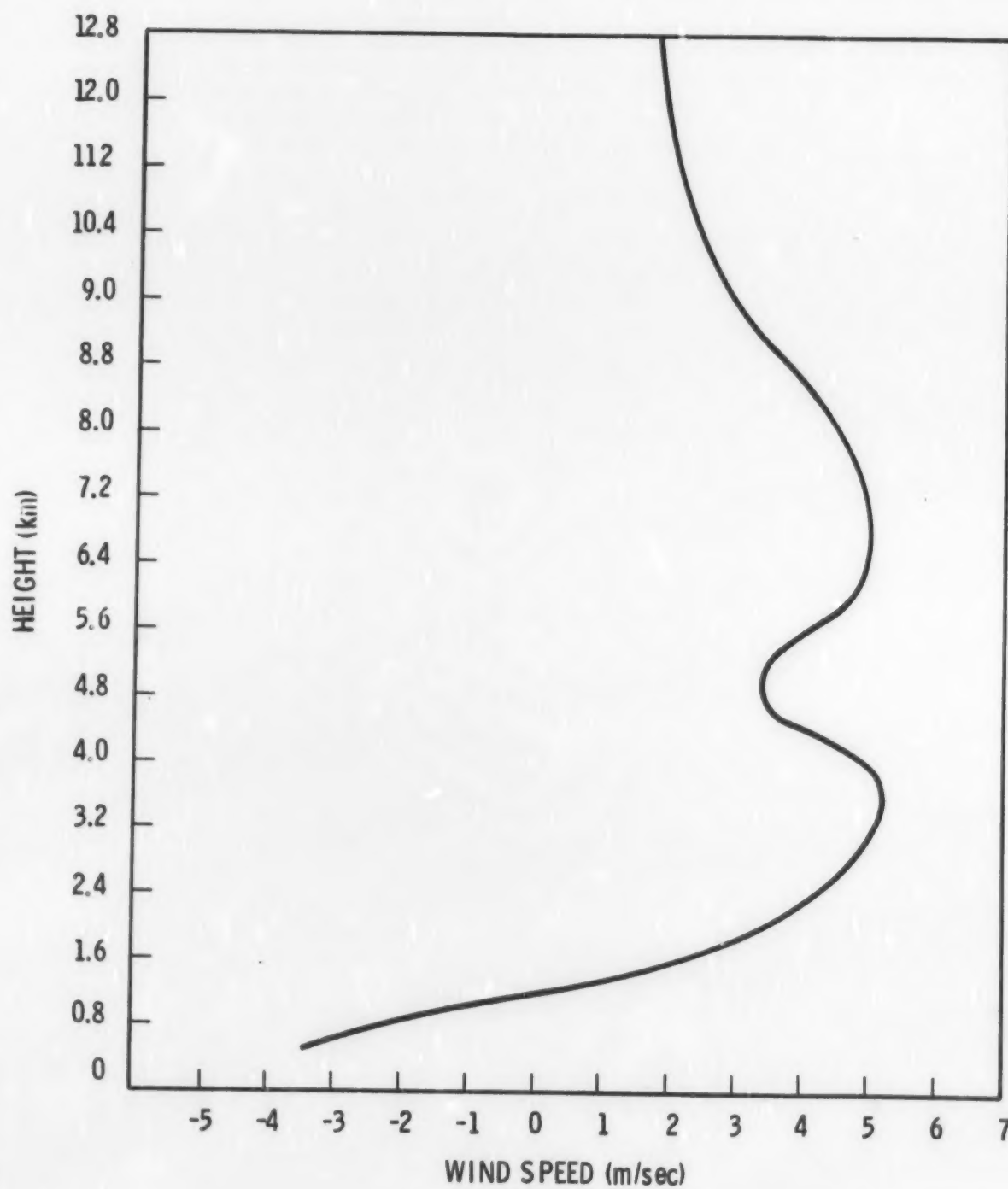


FIGURE 30. COMPONENT OF THE WIND IN THE PLANE OF MOTION OF THE STORM AS A FUNCTION OF HEIGHT FOR THE 21 AUGUST 1972 STORM.

Table 11. VARIABLES OF STATE AND WATER VAPOR MIXING RATIO AS A FUNCTION OF HEIGHT USED AS ENVIRONMENTAL CONDITIONS FOR MODEL CALCULATIONS. BASED UPON OBSERVATIONS TAKEN AT LAMBERT FIELD, ST. LOUIS, MISSOURI ON 21 AUGUST 1972 AT 1417 CST.

Ht. (km)	P (mb)	T (°C)	q_v (g/kg)	ρ (kg/m ³)
0.0	990.	35.2	15.542	1.1082
0.4	947.	30.4	14.526	1.0775
0.8	905.	26.0	13.305	1.0458
1.2	865.	21.6	12.193	1.0147
1.6	826.	17.5	11.503	.9828
2.0	788.	14.0	11.216	.9492
2.4	751.	11.8	8.691	.9134
2.8	716.	8.7	6.264	.8812
3.2	682.	5.7	4.429	.8492
3.6	649.	4.2	4.238	.8130
4.0	618.	2.7	3.825	.7782
4.4	588.	1.1	3.317	.7450
4.8	559.	-1.1	2.707	.7146
5.2	532.	-3.6	2.182	.6861
5.6	505.	-6.9	1.844	.6600
6.0	480.	-9.8	1.511	.6339
6.4	455.	-12.3	1.187	.6075
6.8	432.	-14.6	.896	.5816
7.2	409.	-16.7	.664	.5559
7.6	388.	-18.7	.448	.5312
8.0	368.	-21.1	.377	.5080
8.4	348.	-23.5	.307	.4857
8.8	329.	-25.9	.251	.4641
9.2	312.	-28.3	.207	.4433
9.6	295.	-30.7	.163	.4233
10.0	278.	-33.5	.131	.4045
10.4	263.	-36.3	.104	.3865
10.8	248.	-39.1	.077	.3690
11.2	234.	-42.2	.057	.3525
11.6	220.	-45.4	.045	.3368
12.0	207.	-48.7	.033	.3216
12.4	195.	-52.0	.021	.3069
12.8	183.	-54.2	.015	.2914

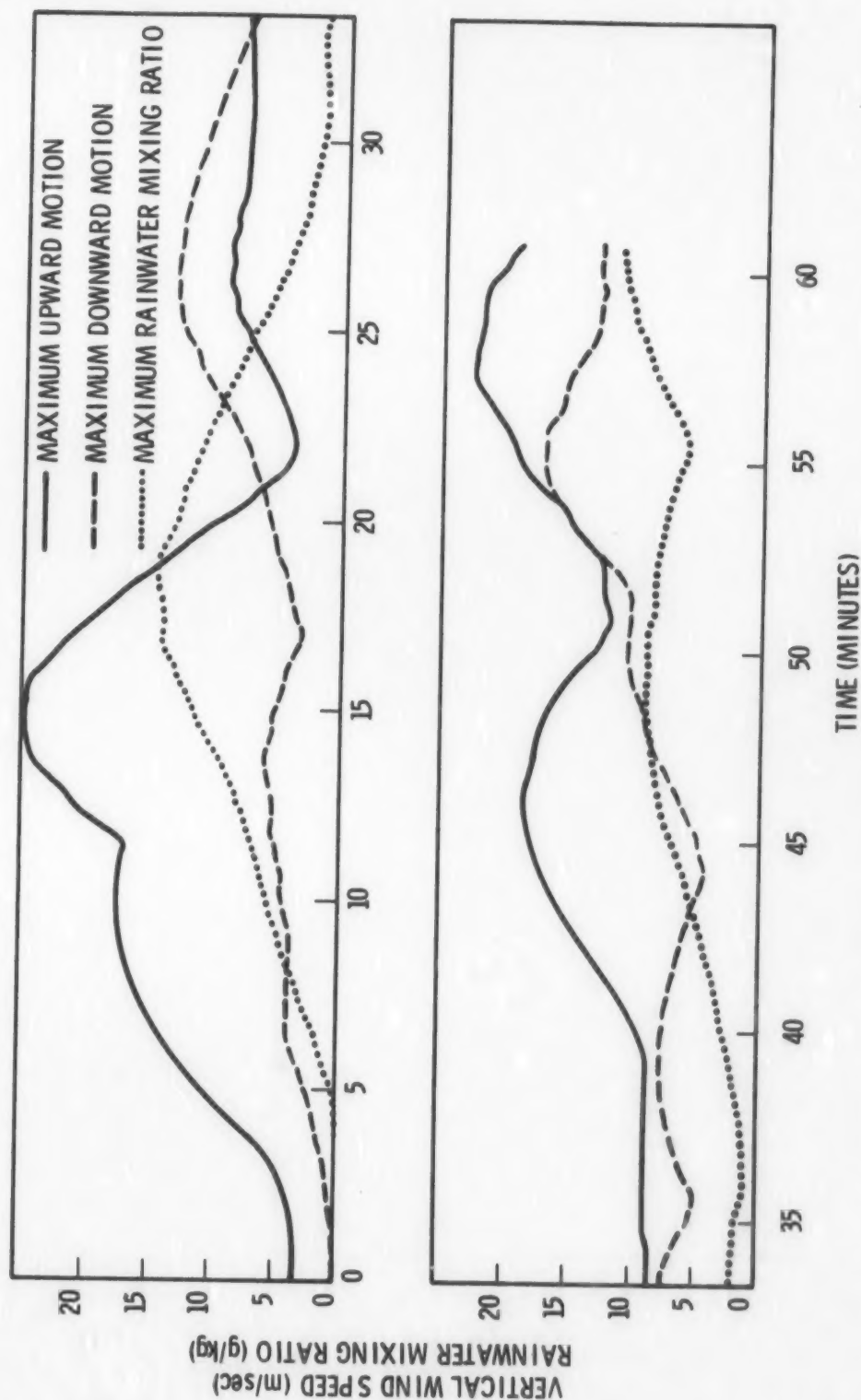


FIGURE 31. TIME EVOLUTION OF MAXIMUM UPWARD MOTION (M/SEC), MAXIMUM DOWNWARD MOTION (M/SEC), AND MAXIMUM RAINWATER MIXING RATIO FOR THE MODEL STORM.

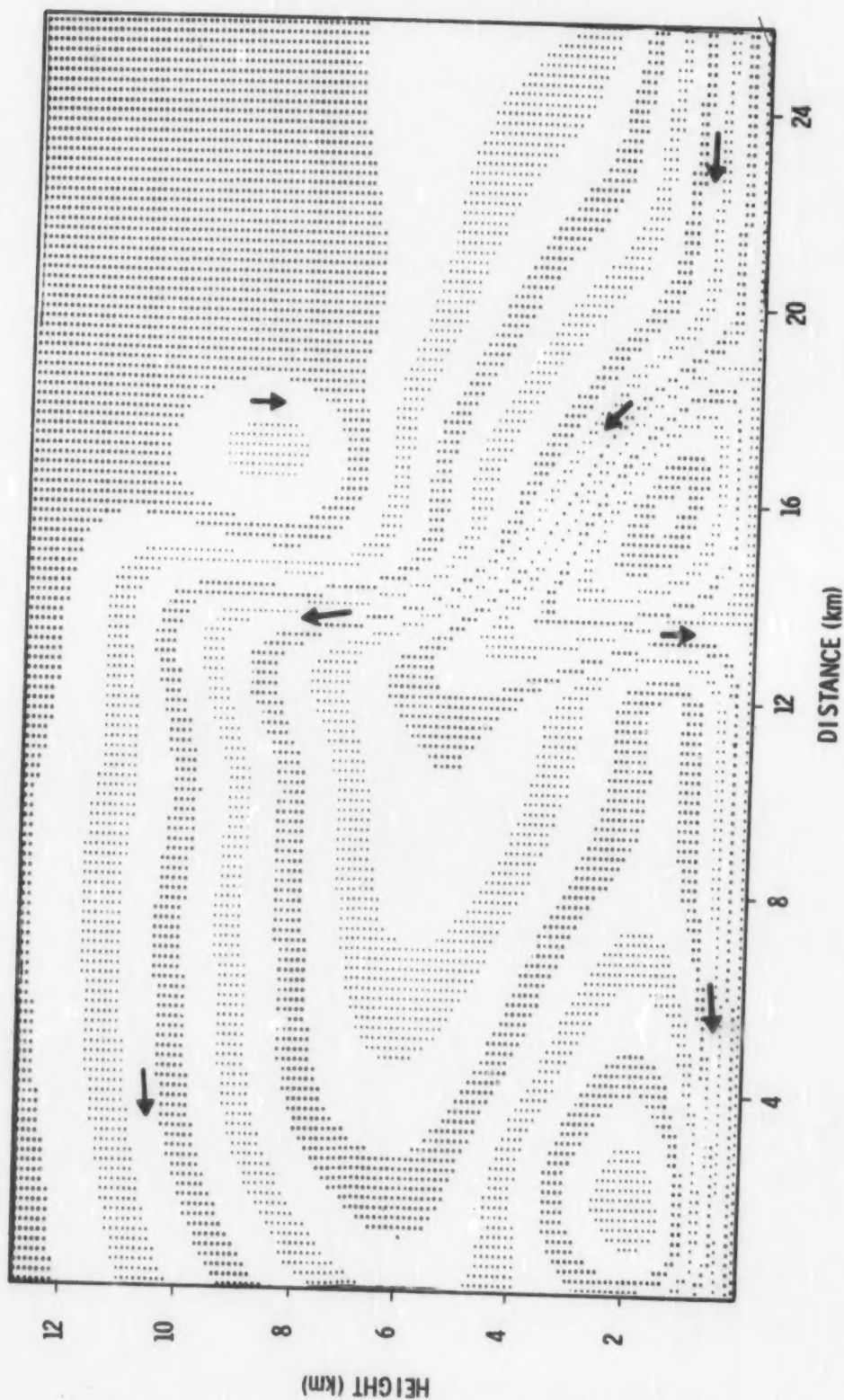


FIGURE 32. THE MOTION FIELD WITHIN THE MODEL STORM AS REPRESENTED BY THE STREAMFUNCTION (KG/M-SEC).

The resulting redistribution of the pollutant by the storm circulation is shown in Fig. 33 at four different times. It can be seen that most of the pollutant is transported to the upper atmosphere while another significant part is retransported to lower levels in the storm downdraft. This portion which is transported to the lower levels would have ample opportunity to be scavenged by cloud and rain since it traverses both the updraft and downdraft. The portion of the pollutant which remains in the upper levels might not be scavenged so effectively. An examination of the circulation pattern within the storm reveals that the air which comprises the downdraft originates in the lowest levels prior to its incorporation into the storm. Therefore, if it is true that pollutant traversing both the updraft and downdraft is scavenged most effectively, the fraction of pollutant which is ultimately scavenged depends to a very large extent upon the vertical distribution of pollutant prior to its entry into the storm.

A next step in this ongoing research will be to determine the extent to which the pollutant traversing various parts of the storm will be scavenged by cloud and rain. This will involve invoking realistic assumptions regarding the interaction of the pollutant with falling rain, and finally assumptions regarding the interaction of pollutant (either as a condensation or as a dissolved gas) with the cloud droplets. Regarding the latter interaction, the pollutant may have to be considered in a less passive manner in its effect upon the evolution of the storm. This approach and others listed in Section IV will be pursued in subsequent stages of this research; the modeling results will form an important part of future reports.

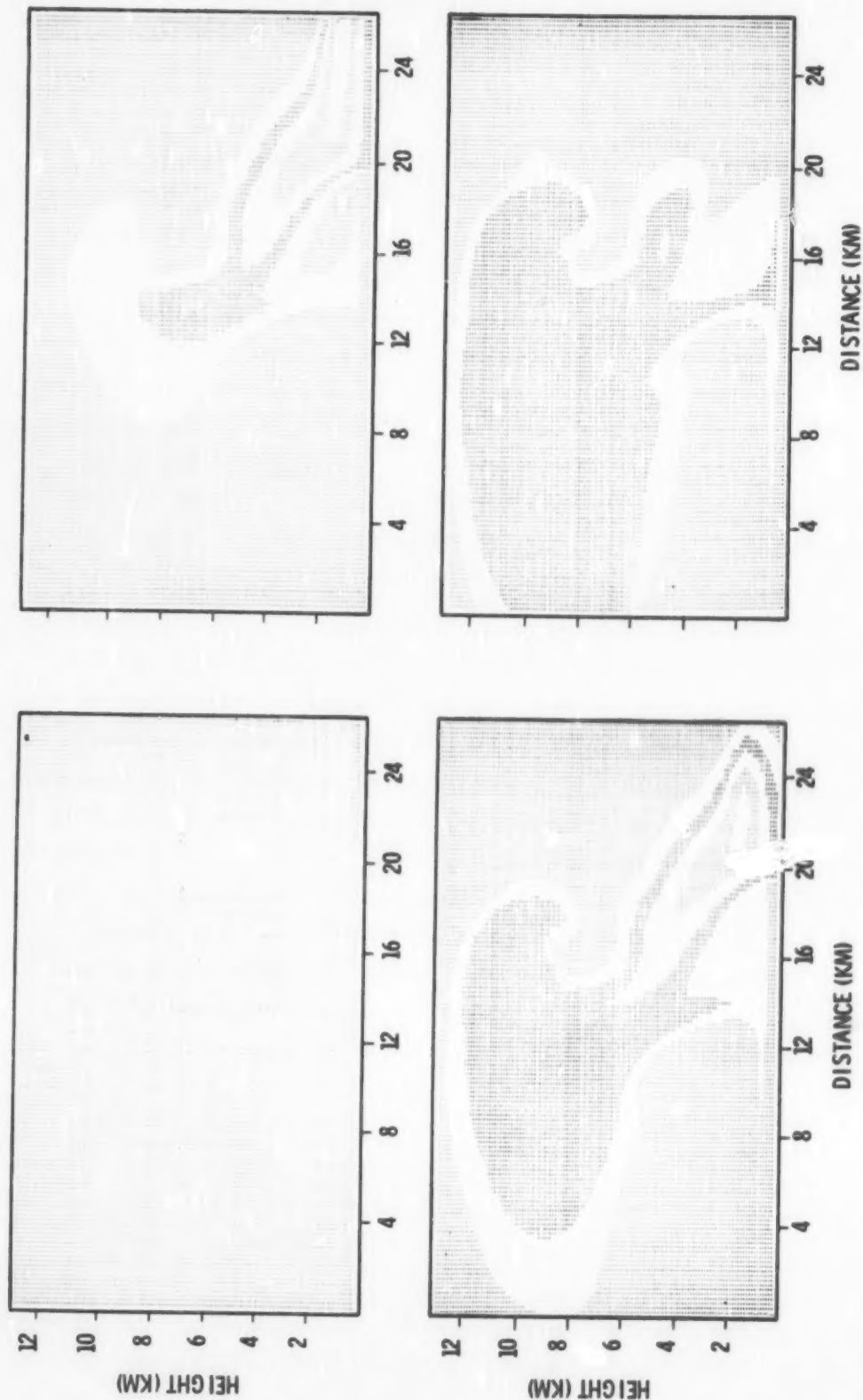


FIGURE 33. THE POLLUTANT DISTRIBUTION AT FOUR DIFFERENT TIMES FOLLOWING ITS INSERTION INTO THE STORM ENVIRONMENT; (Upper left) Time = 0, (Upper right) Time = 30 min, (Lower left) Time = 50 min, and (Lower right) Time = 70 min.

SECTION VIII.

REFERENCES

1. Ludlam, F. H. Severe Local Storms: A Review. Meteorological Monographs. 5(27):33-58, 1963.
2. Newton, C. W. Structure and Mechanism of the Prefrontal Squall Line. J. Meteor. 7:210-222, 1950.
3. Engelmann, R. J. Scavenging Prediction Using Ratios of Concentrations in Air and Precipitation. In: Precipitation Scavenging (1970), Engelmann, R. J., and Slinn, W.G.N., eds. Oak Ridge, Tennessee, USAEC p. 475-485. December, 1970.
4. Engelmann, R. J. Scavenging Prediction Using Ratios of Concentrations in Air and Precipitation. J. Appl. Meteor. 10:493-497, June 1971.
5. May, F. G. The Washout of Lycopodium Spores by Rain. Quart. J. Roy. Meteor. Soc. 84:451-485, 1958.
6. Hales, J. M., J. M. Thorp, and M. A. Wolf. Field Investigation of Sulfur Dioxide Washout from the Plume of a Large Coal-Fired Power Plant by Natural Precipitation. Battelle, Pacific Northwest Laboratories. Richland, Washington. March 1971.
7. Hales, J. M. Fundamentals of the Theory of Gas Scavenging by Rain. Atmos. Environ. (London) 6:635-659, 1972.
8. Hane, C. E. The Squall Line Thunderstorm: Numerical Experimentation. J. Atmos. Sciences. 30:1672-1690, 1973.
9. Scaringelli, F. P., B. E. Saltzman, and S. A. Frey. Spectrophotometric Determinations of Atmospheric Sulfur Dioxide. Anal. Chem. 39:1709, 1967.
10. Lazrus, A., E. Lorange, and J. P. Lodge. New Automated Microanalysis for Total Inorganic Fixed Nitrogen and for Sulfate Ion in Water. In: Trace Inorganics in Water. ACS Advances in Chemistry Series Number 73. Washington, D.C., American Chemical Society, 1968.
11. West, P. W., and T. P. Ramachandran. Spectrophotometric Determination of Nitrate Using Chromotropic Acid. Anal. Chim. Acta. 35:317, 1966.
12. West, P. W. Chemical Analysis of Inorganic Particulate Pollutants. In: Air Pollution, Stern, A. C., ed., New York, Academic Press, 1968.

13. Saltzman, B. E. Anal. Chem. 26:1949, 1954.
14. Dana, M. Terry, J. M. Hales, and M. A. Wolf. Natural Precipitation Washout of Sulfur Dioxide. Battelle, Pacific Northwest Laboratories. Richland, Washington. pp. 23-32. February 1972.
15. Air Quality Data for 1968. U. S. Environmental Protection Agency. Research Triangle Park, North Carolina. APTD-0978. August 1972.
16. Gunn, R., and G. D. Kinzer. The Terminal Velocity of Fall of Water Droplets in Stagnant Air. J. Meteor. 6:246, 1949.
17. Venezia, R., and G. Ozolins. Interstate Air Pollution Study: Phase II Project Report, Part II. Air Pollutant Emission Inventory. USHEW, Public Health Service. Cincinnati, Ohio. December 1966.

SECTION IX.

NOMENCLATURE

Units: l = length; t = time; none = dimensionless

b	Length of sampling line in x direction, l
c_r, c_{rA}	Concentration of pollutant (A) in rainfall from scavenging, moles/ l^3
c_t	Concentration of pollutant in collected rain sample from scavenging and dry deposition, moles/ l^3
d, d_A	Dry deposition flux of pollutant (A), moles/ l^2t
E_2	Efficiency of cloud in removing water from air entering it
f	Fraction of particles which nucleate cloud droplets and are subsequently removed
F	Total flux to surface from both dry and wet deposition, moles/ l^2t
F_{BC}	Fractional removal of pollution between Line B and Line C
H	Height of cloud base, l
i	Subscript: initial, or summation index
J	Rainfall rate, l/t
k_A	Rate of removal of pollutant A from gas phase by hydro-meteors, $t^{-1} l^{-3}$
m_A	Mass of pollutant A in atmosphere, moles
m_f	Mass of material leaving (washout ratio) storm system in air, moles.
m_i	Mass of material entering (washout ratio) storm systems in air, moles
m_{OA}	Initial mass of pollutant A source, moles
m_r	Mass of material leaving (washout ratio) storm system in precipitation, moles

n	Number of precipitation collectors along sampling line
q	Absolute humidity of air entering (washout ratio) storm system, moles/l ³
Q_{OA}	Rate of emission of pollutant A, moles/t
r_A	Generation rate of pollutant A by chemical reaction, t ⁻¹
r_{Ag}	Rate of production of pollutant A in gas phase, t ⁻¹
r_{Al}	Rate of production of pollutant A in liquid phase, t ⁻¹
r_w	Ratio of concentrations of pollutant in water and air at ground level (washout ratio)
t	time
T_r	Time of rainfall at collector site during collection, t
T_t	Total time of sampler deployment, t
U	Mean wind speed, l/t
V	Volume of rain sample, l ³
v_{Ai}	Velocity of pollutant A in gas phase in ith direction (i = x,y,z), l/t
$\bar{v}_{Ag}$	Average velocity of pollutant A in gas phase, l/t
$\bar{v}_{Al}$	Average velocity of pollutant A in liquid phase, l/t
w, w_A	Flux of pollutant (A) to surface by scavenging, moles/l ² t
W	Scavenging rate, moles/l t
x	Distance downwind (or downstorm) from source, l
x_B, x_C	Average distance from St. Louis Arch to Line B, Line C, l
y	Distance across plume (or storm), l
y_i	Coordinate of ith precipitation collector in y-direction, l
z	Height, l

α	Area of precipitation collector, l^2
β	"Reactivity factor" from washout ratio analysis
$\Delta x, \Delta y, \Delta z$	Dimensions of material-balance system in coordinate directions, l
Λ	Washout coefficient, t^{-1}
ρ	Density of water, moles/ l^3
ρ_{Ag}	Molar density of pollutant A in gas phase, moles/ l^3
ρ_{Al}	Molar density of pollutant A in liquid phase, moles/ l^3
x, x_A	Air concentration of pollutant (A) moles/ l^3
Ω	Removal rate by precipitation scavenging, moles/t

SECTION X.

APPENDICES

	<u>Page</u>
A. Field Results for Summer 1973	93
B. Some References Pertinent to the Field of Precipitation Chemistry	121

Preceding page blank

APPENDIX A: FIELD RESULTS FOR SUMMER 1973

As noted in the introduction to this report, unanticipated changes in program planning have led to the temporary discontinuation of this project. Consequently the results for the summer 1973 field period are presented here in rather brief form, hopefully for the benefit of others who may be conducting future research in this area. These results are composed primarily of rain-concentration and sounding information. Detailed synoptic material is currently on file at BNW but has not been included in this Appendix.

The study of precipitation scavenging mechanisms affecting removal of metropolitan-source pollutants proceeded with a second summertime field program in the St. Louis area. As during the August, 1972 effort, rain samples from convective storms were collected and chemically analyzed for several pollutant species. Support operations included rawinsonde releases, aircraft measurements, and radar observations. A considerably expanded field operation was successfully maintained, however, through a cooperative effort with other Battelle projects in the area. Extension of the spatial and temporal capabilities of the sampling array, plus additional aircraft flights with more instrumentation allowed us to add a considerable body of experimental results which will prove beneficial in ongoing precipitation scavenging model development and testing. This appendix describes progress in collection and analysis of data from the July, 1973 field work, and initial developments in the modeling program.

Experimental Procedure

With the exception of the additions described below, the procedure for collection of rain samples and meteorological data was the same as during the August, 1972 field program. The field director at Lambert Field National Weather Service station (STL), observed the meteorological radar and alerted the field crew for deployment of samplers in anticipation of rainfall. The sampling array, which consisted of three sampling lines in 1972, was expanded to form the grid of 120 sample positions shown on

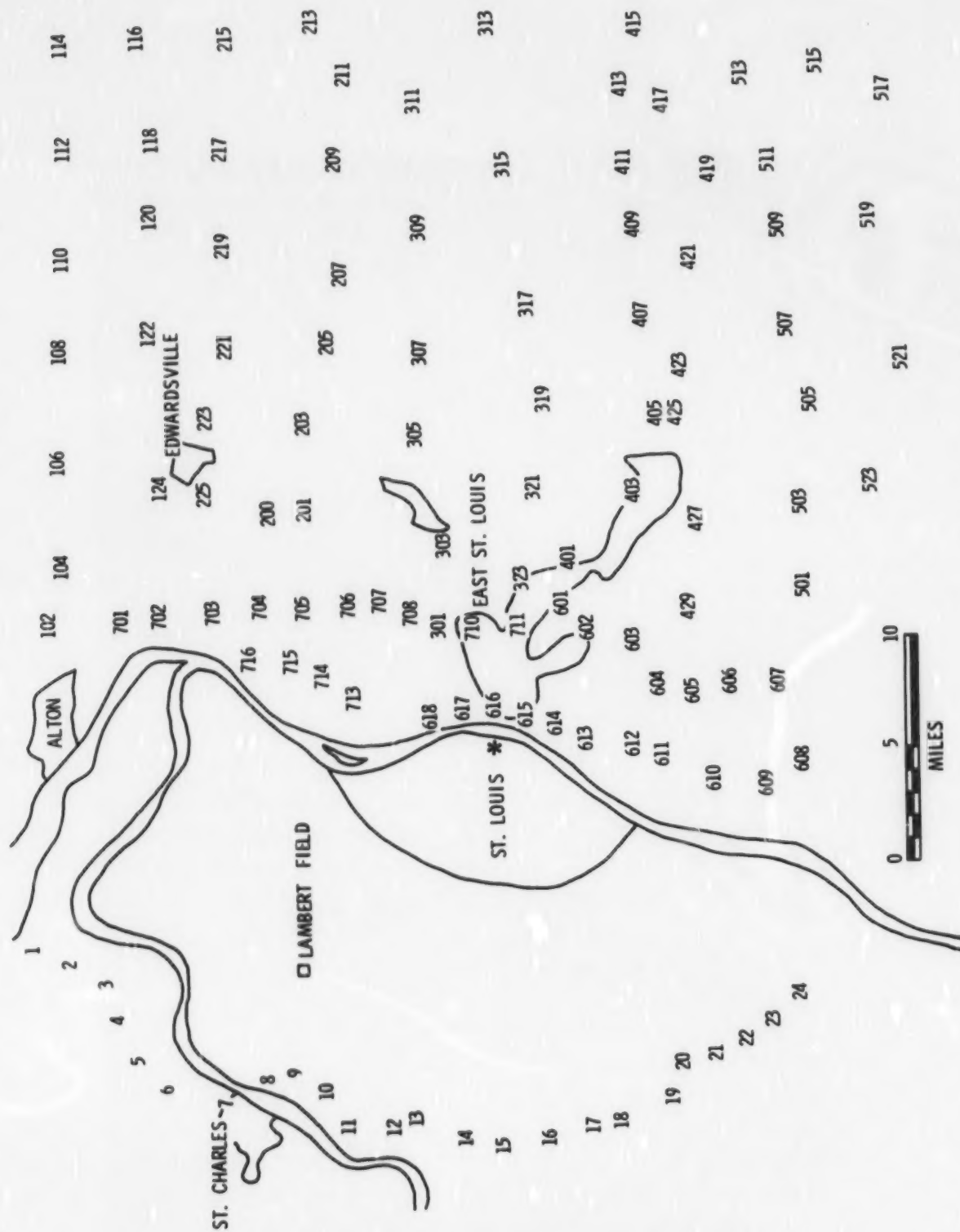
page 95. This new network included the original western (upstorm) line, plus a downstorm grid which extended from 2 to 52 km east of the St. Louis Arch ("*" on figure). Maintenance of this extended array was achieved through cooperation with a concurrent Atomic Energy Commission research effort, which employed several students as field workers in addition to Battelle personnel. The additional manpower allowed essentially all the sampling positions to be maintained on each storm day. We had found in 1972 that the dry ice freezing rain collectors remained effective for several hours prior to rainfall; thus the entire grid could be set out during the mornings of likely storm days. We then were able to operate with a minimum of short-term forecasting of storm direction and speed.

Short-term forecasting was used, however, for directing the placement of a sequential rain collector, new this year. The sampler, shown on page 96, consisted of a 1 m^2 plastic funnel mounted on an automobile. Sufficient rainwater to constitute a sample could be collected over time intervals as short as 30 seconds. The sampler was directed--when time allowed--to near the center of the anticipated rainfall pattern; in all three cases of use, samples were taken from the onset of rain through the duration of the shower.

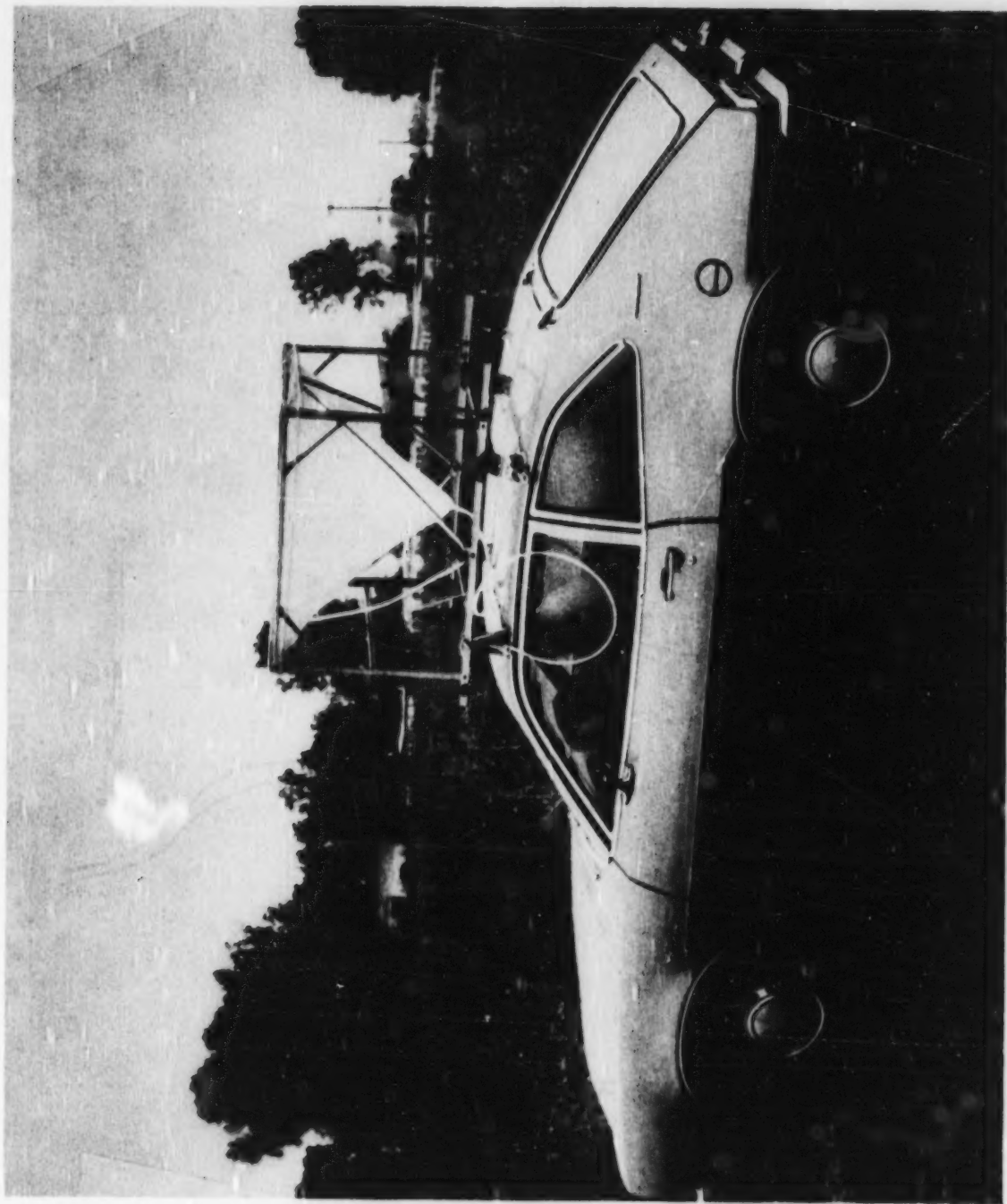
Another addition to the field operations was a radio system which allowed near-continuous contact between the field director and most of the field crew. Contact was also maintained with personnel at the METROMEX radar center at Pere Marquette State Park, Illinois, and thus with operating aircraft and forecasters. This communication link was deemed useful in coordinating field operations and forecasting among all the active researchers.

Precipitation Scavenging Results

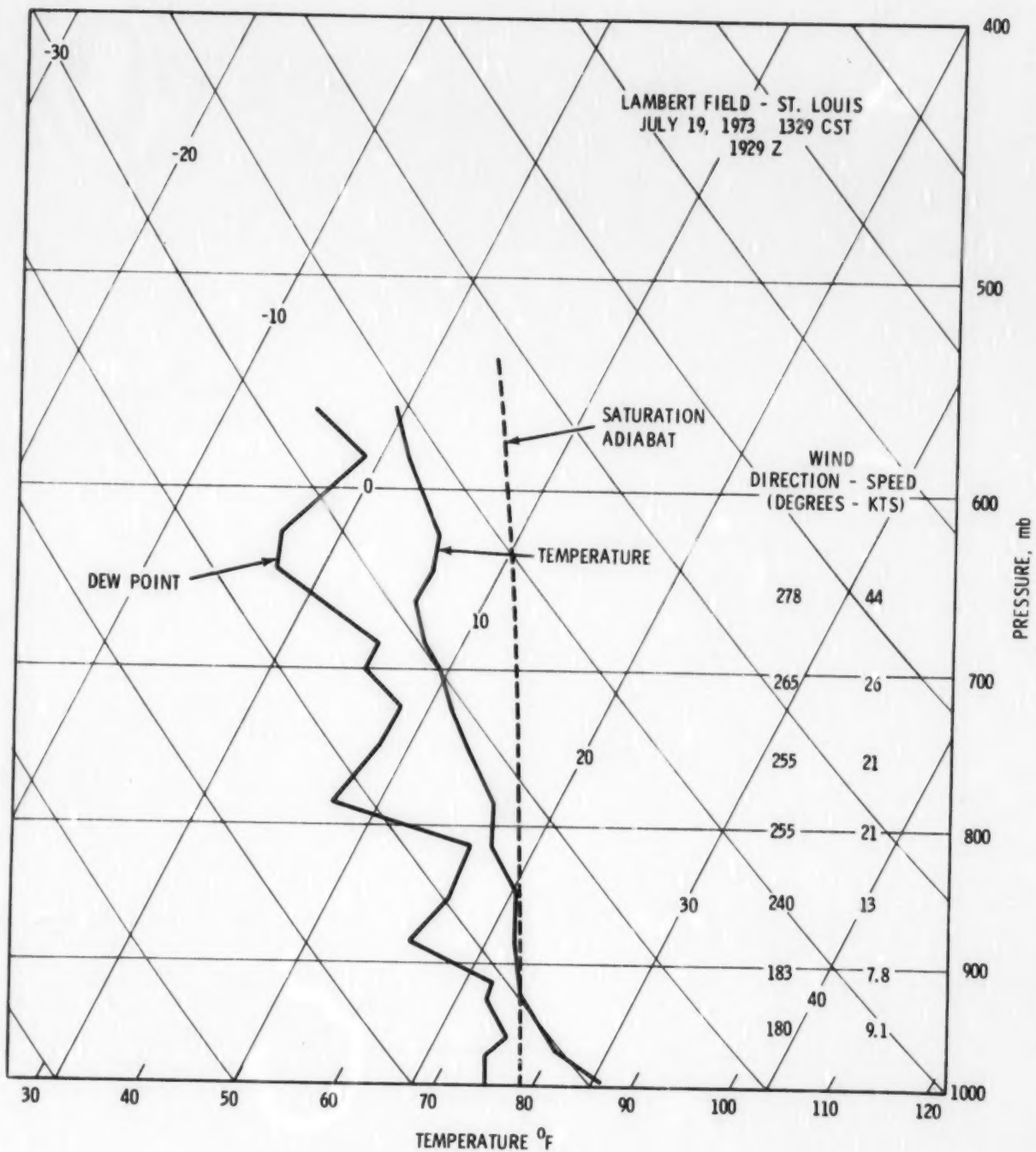
The table on page 103 lists general data on the storms sampled during the field period of July 9-July 27, 1973, plus radiosonde release times and remains on the various runs. Temperature-dew point profiles and wind data resulting from the radiosonde flights are shown in figures, pages 97-102. As was the case with the 1972 field program, much of the rainfall was associated with quasi-frontal or squall-line activity, and the rainfall



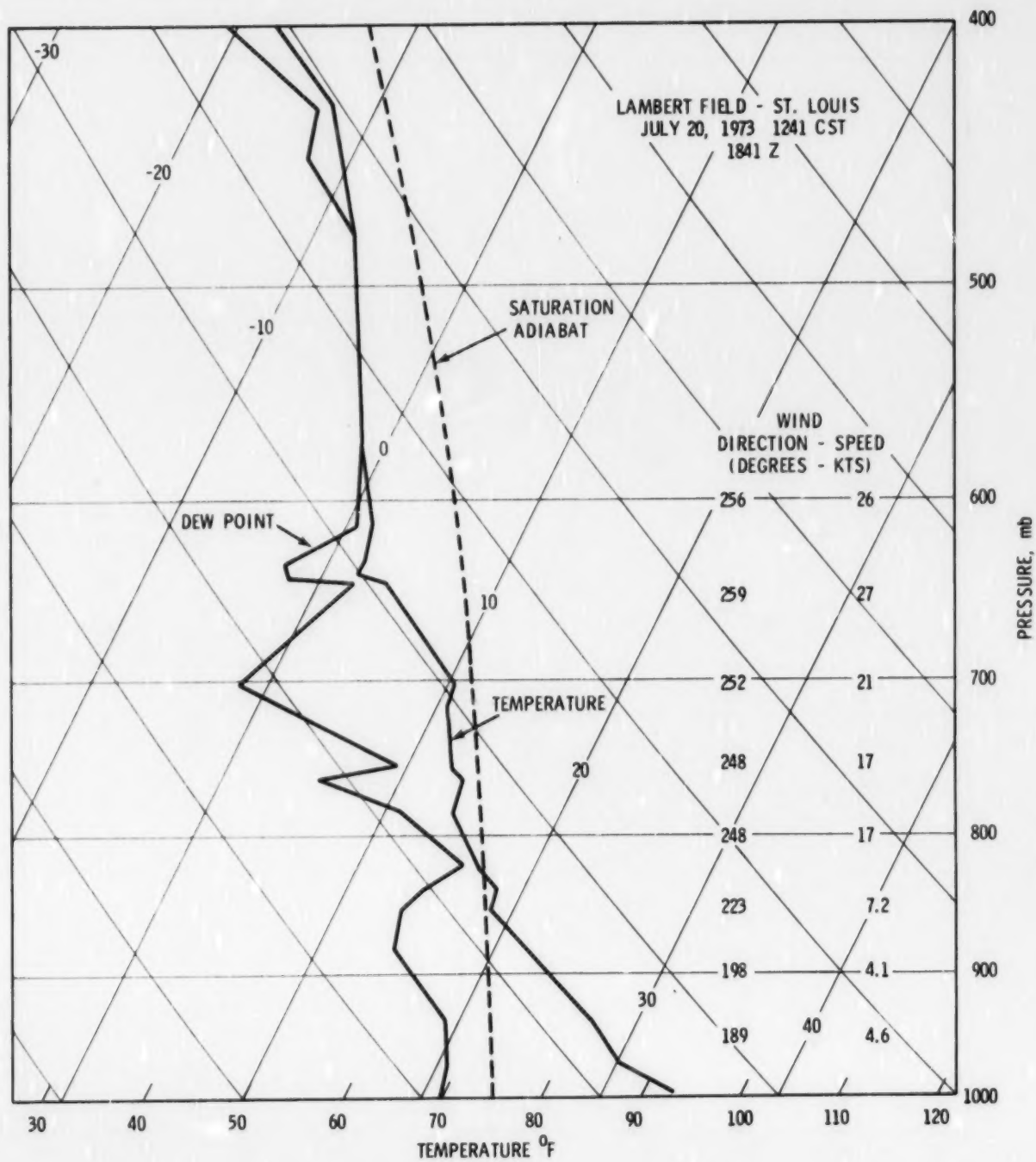
JULY, 1973, PRECIPITATION SAMPLING ARRAY.



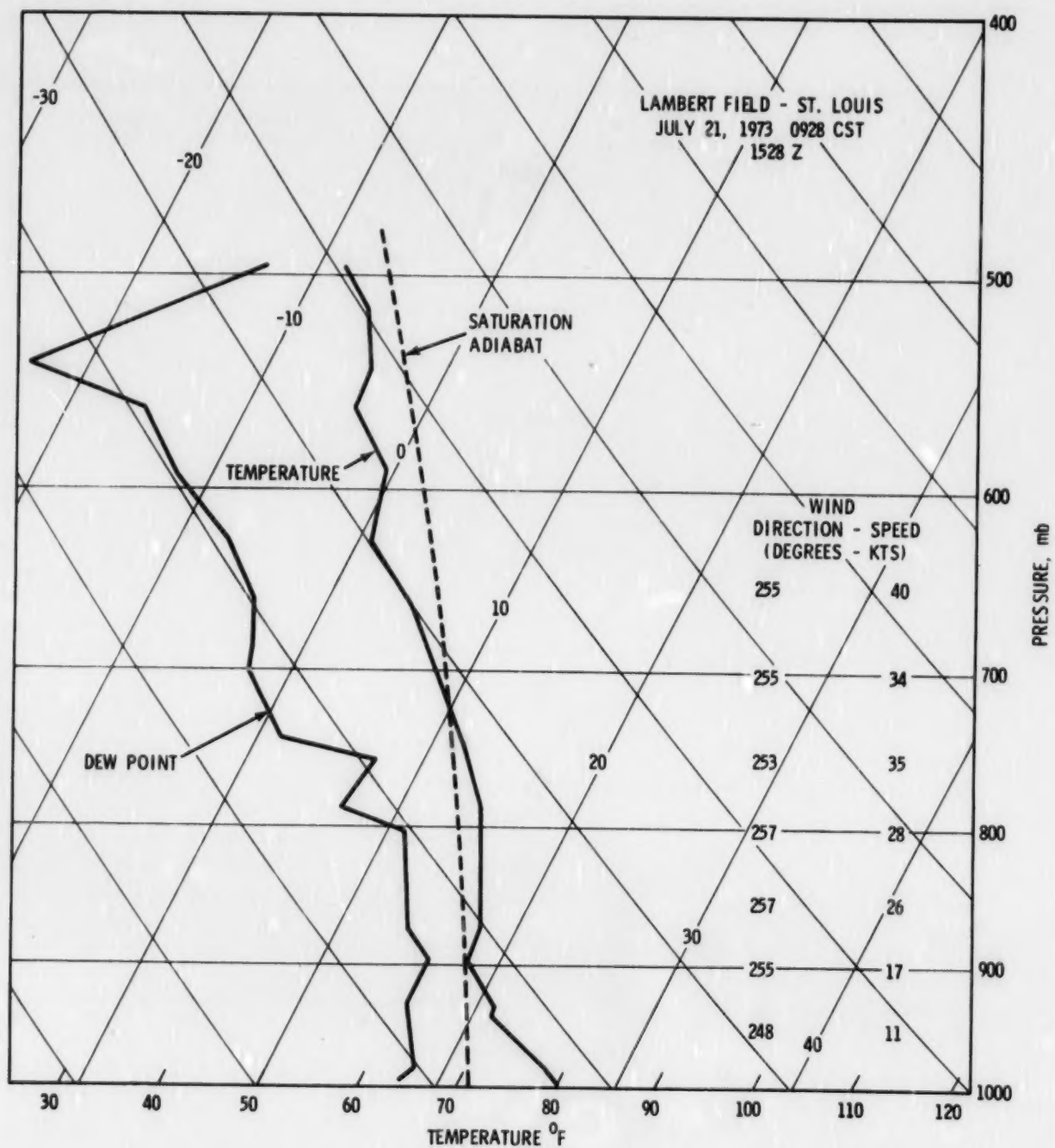
SEQUENTIAL RAIN SAMPLER.



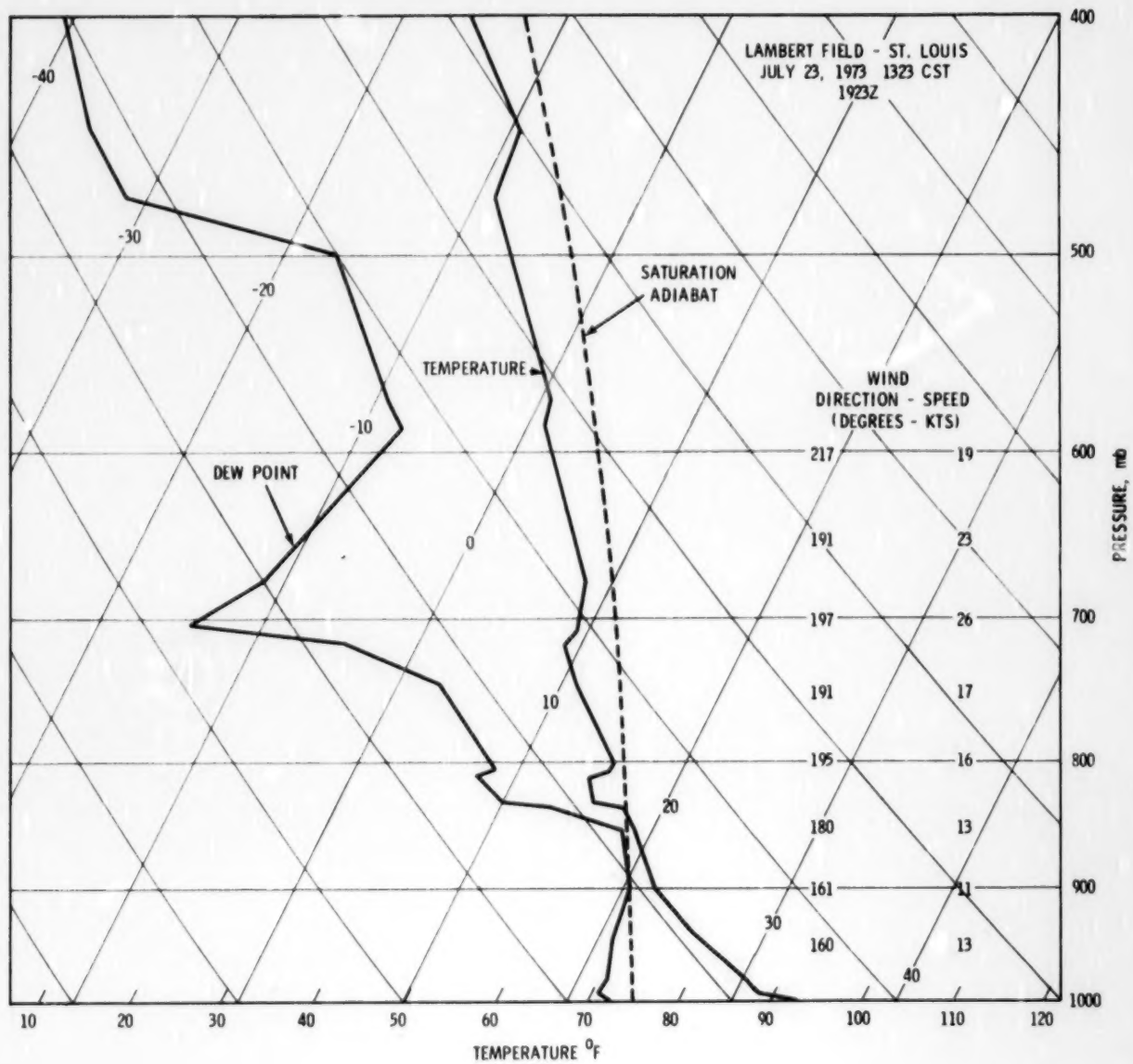
JULY 19, 1973 RADIOSOUNDING



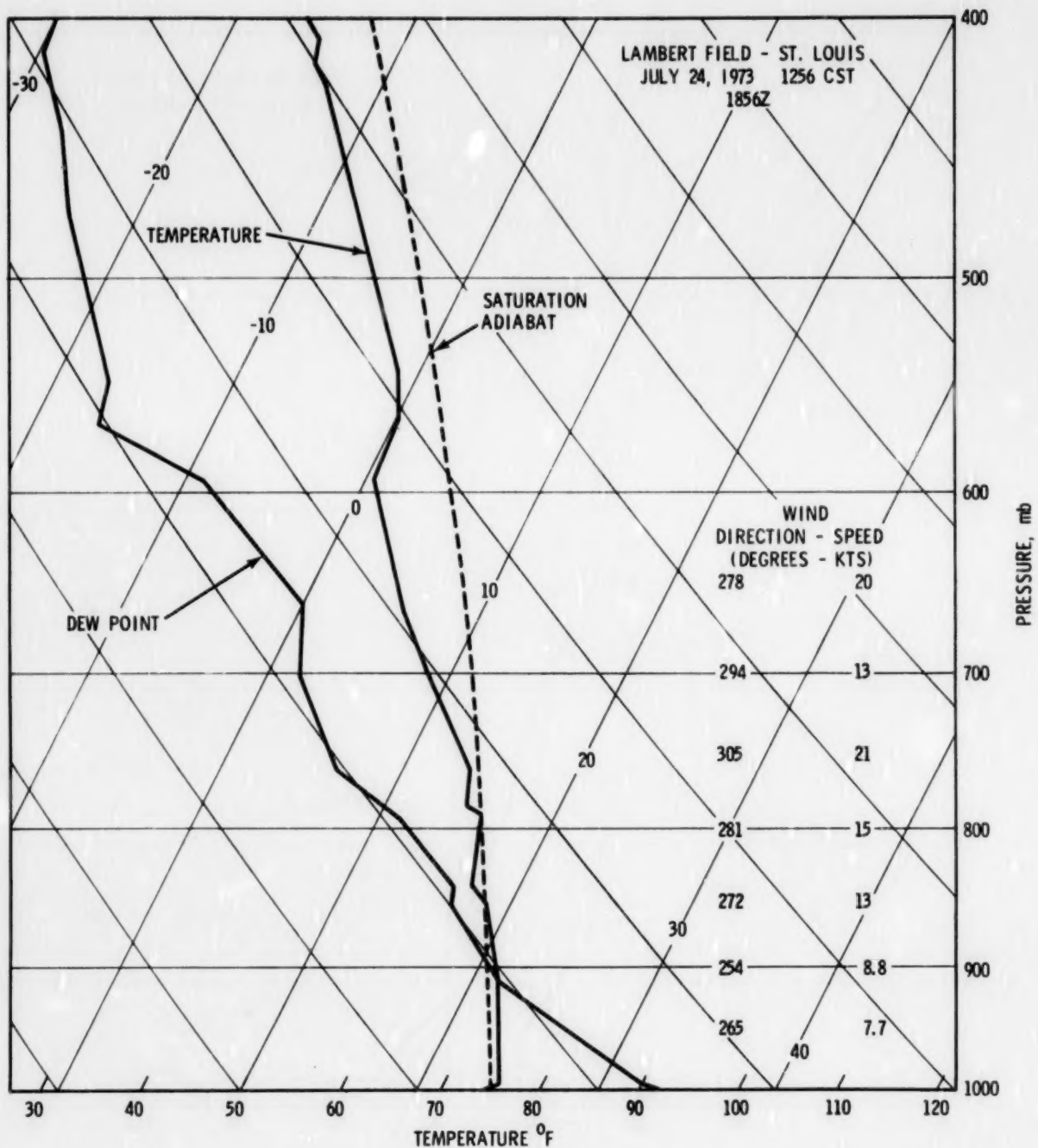
JULY 20, 1973 RADIOSOUNDING



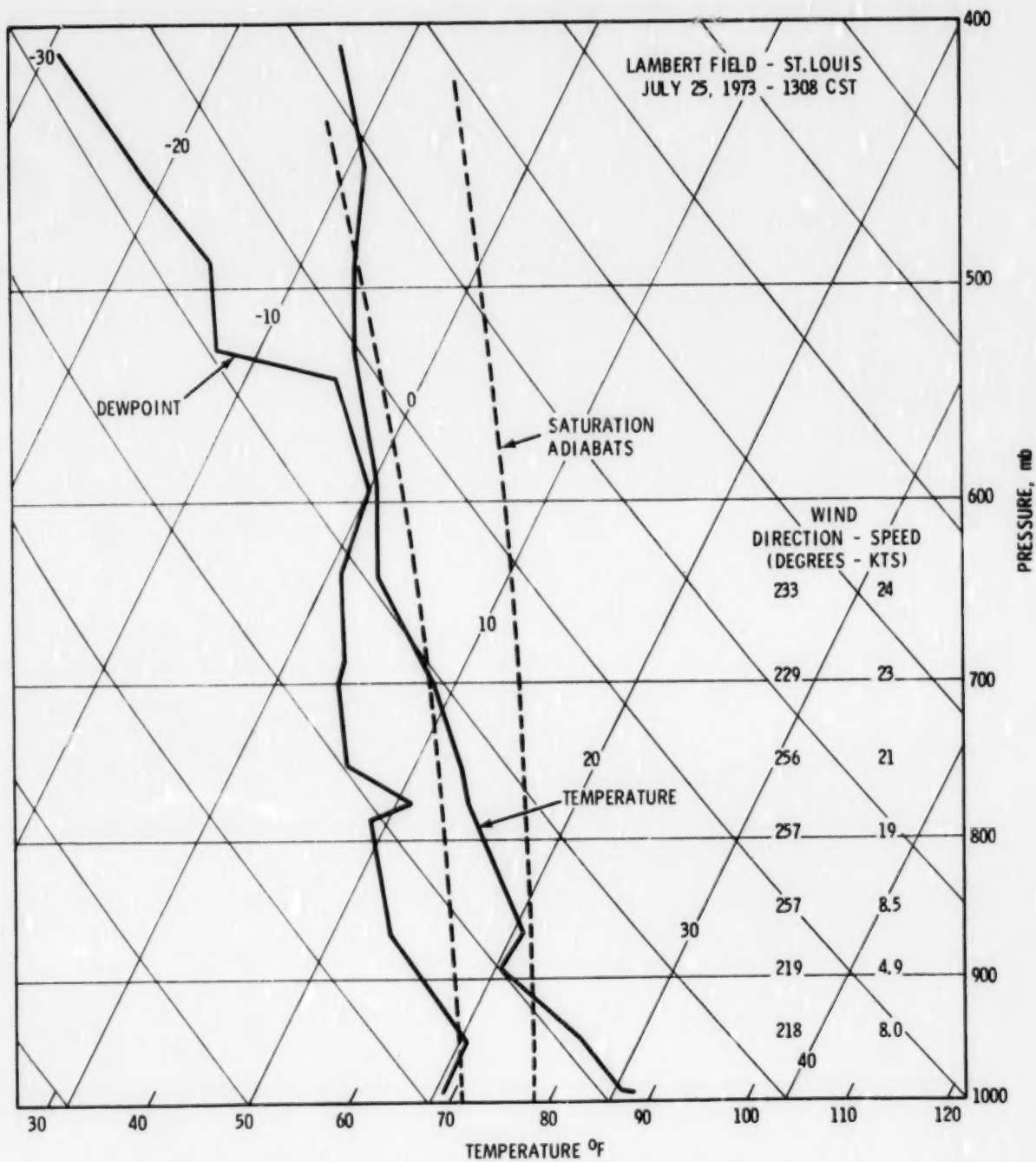
JULY 21, 1973 RADIOSOUNDING



JULY 23, 1973 RADIOSOUNDING



JULY 24, 1973 RADIOSOUNDING



JULY 25, 1973 RADIOSOUNDING

GENERAL DATA: INORGANIC POLLUTION SCAVENGING OPERATIONS--1973 FIELD STUDY

Date	Run No.	Sampling Coverage ^a	Total No. of Samples	Approx. Time of Rainfall (CST)	Radioonde Release Time (CST)	Remarks
7-14-73	6	0, 4-7	24	1600-1800		Most samples frozen - immediate recovery.
7-18/19-73	7	0-7, S301 ^b	90	0800-1000	1329 (7-19)	Overnight collection - most unfrozen.
7-20/21-73	8	0	10	Early AM 7/21	1241 (7-20) 0928 (7-21)	No useable samples saved.
7-23-73	9	0-7	89	Early AM		Overnight - all unfrozen, immediate collection.
7-23-73	10	0-7, S301 ^b	79	1500-1900	1323	Same day collection - most frozen.
7-24-73	11	0-7	4	1300	1256	Isolated shower - all frozen.
7-25-73	12	3-6	14	Early PM	1308	Same day collection - most frozen.
7-25-73	13	S200	8	2100-2200		Sequential - all frozen.
7-25/26-73	14	0-3, 6-7	59	Late PM 7/25		Overnight - most unfrozen.

^a Sampler groups are identified by the first digit of the sample position number.

^b Sequential samples taken at position indicated.

was often spread over the majority of the sampling area. The sampling groups (located on Figure 33) are identified by the first digit to the sampling position number. Four of the nine runs involved overnight collections, as we followed the policy of leaving the sampling stations equipped at all times. This policy proved feasible after several unsuccessful storm days early in the field series left us with the samplers deployed at night-fall. The remarkable lack of vandalizing of samplers prompted us to take advantage of overnight collections. However, the overnight collections were generally unfrozen at pickup because of dissipation of dry ice. There were notable exceptions which confirmed the ability of the samplers to remain effective even after long setout times: the four samples of Run 11 (a very isolated shower) were collected frozen despite 24 hours of exposure. The runs of July 25-26 are numbered loosely on the basis of pickup times; many separate showers were sampled during that period, and final sorting will have to await analysis of data from the raingage network maintained by Illinois State Water Survey.

The chemical analyses for the species SO_2 , SO_4^{--} , NO_2^{--} , NO_3^- , NH_4^+ , and H^+ were conducted during the two-month period following the field trip. All samples had been kept frozen and shipped by air to Richland, Washington. Our decision to confine the analyses to our home laboratory rather than in the field have proved beneficial, as the analysis of some 400 samples would not have been nearly completed during the field period. The measured concentrations of pollutants are listed in tables, pages 105-119. Many notes were taken regarding unusual aspects of the collection (such as evidence of tampering, frozen or unfrozen, etc.); these have not been fully evaluated, but certain samples are merely noted at this time as being suspicious. Thus the concentration data should be currently regarded as rather raw, pending further examination of sampling conditions, possible degradation of the samples due to exposure at ambient temperature, etc.

Initial observations of results of repeated analyses seem to indicate that our original fears regarding loss of ammonium ion and chemical reaction of other constituents may have been largely unfounded. Further study is necessary, but it appears that exposure to room temperature for up to two days

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 6, JULY 14, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
014	0.11	0.46		0.48	97.0	61.0	2.8
015 ^a	0.40	0.70	78.1	0.31	55.3	54.7	15.5
016	0.05			0.30	145.	64.5	
401	0.13	0.82	175.	0.27	180.	81.8	35.5
405	0.09	0.48		0.51	179.	72.0	25.7
407	0.10	0.48		0.26	214.	82.1	95.5
411	0.03			0.35			
417	0.04			0.45			
419	0.05			0.31	143.	35.9	
421	0.08			0.39	130.	34.1	<10.
423	0.08			0.28	143.	54.4	58.9
501	0.59		72.9	0.11			
503	1.04	0.95	76.0	0.15	36.4	47.0	309.
505	0.34	0.85	155.	0.22	109.	91.1	89.1
521		0.24	74.0		50.	57.0	63.1
601	0.05			1.08			
602	0.25	0.41	145.	0.40	142.	59.3	13.8
603	0.45	0.38	124.	0.27	119.	62.2	12.6
604A	0.51	0.85	113.	0.27	72.2	41.8	60.3
604B	0.65	0.38	88.5	0.15	66.9	51.1	64.6
605	0.73	<.2	98.9	0.12	52.0	34.5	89.1
606 ^a	1.25	1.45	68.8	1.15	61.9	44.1	<10.
607	0.71	0.26	75.0	0.05	55.2	50.8	102.

^a Questionable quality - see text.

CONCENTRATIONS OF INORGANIC NONMETALLIC
POLLUTANTS - RUN 7, JULY 18-19, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
007	0.08	1.26	88.5		82.0	14.7	9.5
008	0.13	1.37	62.5		28.5	8.2	47.9
009	0.20	0.46	58.3	0.60	32.9	7.8	30.2
010	0.25	0.59	65.6	1.18	33.9	3.1	7.6
011	0.24	0.39	55.2	0.46	37.1	7.6	38.9
012	0.29	0.90	61.5	0.67	26.0	14.7	23.4
013	0.27	<.1	44.8	0.41	28.8	11.6	29.5
014	1.42	<.1	12.5	0.10	9.3	10.1	37.2
015	1.17	<.1	15.6	0.11	12.9	8.8	35.5
016	1.18	<.1	29.2	0.07	13.8	11.6	66.1
017	0.80	<.1	57.3	0.20	16.2	16.9	77.6
018	0.74	<.1	50.5	0.74	16.6	9.9	36.3
019	0.74	<.1	56.8	0.09	14.3	14.9	95.5
020	0.76	<.1	34.4	0.06	22.6	19.4	39.8
201 ^a	0.15	1.23	68.0	0.72	42.6	36.1	0.4
203 ^a	0.10	1.52	125.				24.0
205	0.09	1.14	81.5		30.7	14.7	58.9
301	0.75	0.21	44.8	0.07	41.3	14.1	15.8
303	0.26	<.2	55.2	0.11	48.6	10.2	58.9
305	0.21			0.63	29.8	13.2	17.8
307	0.21	<.2	31.1	<.1	55.6	12.8	74.1
315	0.21			0.18	42.0	14.1	24.5
317	0.79	<.2	46.0	0.10	43.2	25.2	44.7
319	1.36	<.2	71.6	<.1	38.7	21.3	105.
321	0.41	0.22	67.2	0.56	53.5	12.2	309.
323	0.33			0.67	28.7	10.1	12.3
403	0.72	0.64	53.1	0.07	29.6	11.5	5.6
405 ^a	0.88	1.02	111.	0.07	51.2	23.2	120.
407 ^a	0.31	0.20	102.	0.08	52.4	13.5	91.2
409	0.63	0.98	97.9	0.19	64.8	28.5	129.
411	0.57	0.31	44.8	0.08	37.5	14.7	64.6
413	0.42			0.10	20.9	7.8	105.
415	0.30			0.16	30.5	16.9	29.5
417	0.39	0.35	71.9	<.1	36.8	8.9	123.
421 ^a	1.21	0.31	62.5	0.07	36.8	15.4	63.1
423 ^a	1.57	0.68	74.5	0.16	27.0	22.6	110.
425 ^a	0.35			1.62	31.0	9.9	2.5
427	0.72			0.75	27.8	15.2	2.0

CONCENTRATIONS OF INORGANIC NONMETALLIC POLLUTANTS -
RUN 7, JULY 18-19, 1973. (Continued)

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
501 ^a	1.61	<.2		<.1	13.6	17.1	35.5
503	1.49	<.2	36.5	<.1	18.6	10.9	40.7
505	1.53	<.2	32.3	<.1	12.5	7.7	30.2
507	0.79	0.21	64.6	0.09	34.0	9.6	102.
509	1.06	0.24	47.9	0.08	33.0	21.3	87.1
511	1.18	<.2	44.8	<.1	30.9	16.7	95.5
513	0.86	0.31	61.5	0.51	18.9	10.8	8.1
515	0.39			0.08	26.0	12.8	112.
517	0.78	0.67	40.9	0.12	30.6	22.2	63.1
519	0.47			0.22	21.7	17.1	50.1
521	1.26			0.08	16.7	13.2	69.2
523	0.33	0.40	44.8	0.09		20.0	37.2
601 ^a	0.17	<.1	72.7	0.33	21.5	17.8	23.4
602	0.27	<.1	87.5	0.35	31.8	3.5	50.1
604	0.18	<.1	66.7	0.41	33.7	9.3	41.7
605	0.18	<.1	85.4	0.45	52.6	6.5	45.7
607	1.38	<.1	27.2	<.1	11.7	17.8	61.7
608	0.23	<.1	42.2	0.58	20.3	14.7	53.7
610	0.28	<.1	44.0	0.46	50.6	8.2	1.6
611	0.31	<.1	64.1	0.29	44.4	5.6	45.7
612	0.39	<.1	55.2	0.45	37.1	8.8	46.7
613	0.42	<.1	46.0	0.33	30.9	5.2	15.1
614	0.37	<.1	58.9	0.57	28.2	30.3	53.7
615	1.14	<.1	44.8	0.20	20.8	6.9	60.3
616 ^a		<.1	37.5			8.0	8.1
617 ^a	1.6	<.1	16.7			16.7	10.2
703 ^a	0.03						
704 ^a	0.08		115.	1.65	91.2	1.7	
705	0.15		79.0	1.22	68.1	3.5	25.7
706	0.22		62.5	0.87	54.1	9.3	10.2
707	0.28		73.4	0.74	48.2	6.1	31.6
708	0.35		72.7	0.61	55.9	6.9	12.0
710	0.65		40.6	0.31	25.5	7.6	24.0
711	0.38		55.7	0.32	21.7	2.7	30.9
713	0.31		72.4	0.92			38.0
714 ^a	0.29			0.85			24.5
715	0.16			0.74			47.9
716	0.08				88.6	15.4	

^a Questionable quality - see text.

SEQUENTIAL SAMPLE CONCENTRATIONS OF INORGANIC
NONMETALLIC POLLUTANTS - RUN 7, JULY 18-19, 1973.

Sample Position (Sequential)	Rainfall Rate cm/hr	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
A	0.62	<.1	24.5	0.35	33.7	15.2	36.3
B	0.57	<.1	49.5	0.07	18.2	9.5	145.
C	0.58	<.1	39.6	0.06	16.9	13.2	123.
D	0.16	<.1	44.8	0.07	33.6	24.2	126.
E	0.28	<.1	27.1	0.07	44.7	36.1	100.
F	0.13	<.1	55.2	<.06	40.5	24.9	162.
G	0.06	<.1	68.8	0.09			
H	0.22	<.1	50.5	<.06	26.3	15.6	145.
I	0.36	<.1	19.8	<.06	11.7	8.8	97.7
J	0.49	<.1	29.2	<.06	7.7	4.6	95.5
K	0.53	<.1	28.1	<.06	6.5	2.7	105.
L	0.26	<.1	63.5	0.09	23.2	11.2	95.5
M	0.08	<.1	50.5				
N	0.04	<.1	32.3	0.08	19.6	10.3	75.9

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 9, JULY 23, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) $\times 10^6$					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
008	0.56	0.24	23.0	<.1	29.5	3.5	17.8
009	0.63	<.2	23.6	<.1	28.5	5.8	24.5
010	0.76	<.2	22.6	0.47	24.7	3.0	7.6
011	0.70	0.22	37.6	<.1	27.3	6.5	37.2
012	0.86	<.2	18.3	0.41	26.4	2.7	10.5
013	0.83	0.24	10.0	<.1	26.5	3.6	16.2
014	0.84	<.2	14.5	<.1	24.5	2.1	45.7
015	0.85	0.26	11.6	<.1	25.7	3.0	10.2
016	0.85	<.2	13.2	0.31	23.6	1.7	12.0
017	0.84	0.78	20.4	0.14	24.7	8.6	28.2
018	0.89	<.2	16.0	0.35	22.3	3.5	6.5
019	0.89	<.2	17.1	<.1	20.3	6.5	63.1
020	0.90	<.2	13.2	<.1	24.4	5.1	32.4
102 ^a	0.28	<.2	48.3	<.1	44.1	6.5	141.
104	0.23	<.2	76.4	0.39	57.7	7.1	89.1
106	0.18	<.2	83.1	0.08	68.8	51.2	151.
108	0.21	0.63	83.9	0.75	70.9	67.1	17.8
110	0.26	<.2	55.3	0.24	55.1	6.2	5.6
112	0.62	0.63	39.4	0.25	32.2	61.0	16.2
114	0.35	<.2	39.8	0.08	47.7	23.9	102.
116	0.38	<.2	54.9	0.14	48.3	18.6	95.5
118	0.34	<.2		<.1	50.6	22.7	97.7
120	0.51	<.2	40.3	0.07	41.3	22.9	81.3
122	0.36	<.2	67.5	0.11	51.4	14.4	70.8
124	0.30	<.2	53.1	0.09	51.9	5.0	35.5
201	0.51	0.36	46.3	0.65	49.9	25.8	38.9
203	0.25	<.2	41.7	0.09	56.4	9.9	56.2
205	0.37	0.56	57.0	0.06	59.1	20.3	36.3
207	0.97	1.01	33.4	0.68	53.0	17.1	10.5
209	0.70	<.2	18.8	.06	28.7	12.1	56.2
211	0.66	<.2	24.4	0.11	45.3	25.4	33.9
213	1.19	0.81	23.7	0.55	27.6	1.5	4.5
21	0.57	5.08	33.1	0.29	23.7	45.1	120.
217	0.38	<.2	30.4	0.11	39.0	8.0	70.8
219	0.76	<.2	30.0	0.06	26.1	9.0	40.7
221	0.37	<.2	24.4	0.08	35.4	7.1	70.8
223	0.42	0.35	39.6	0.12	42.3	16.7	30.9
225	0.33	<.2	55.6	0.14	57.3	12.3	56.2

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 9, JULY 23, 1973. (Continued)

Sample Position	Rainfall cm	Concentration (gm-moles/l) $\times 10^6$					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
301	0.66	0.36	43.6	0.67	44.9	14.3	35.5
303	0.86	<.2	34.9	0.09	35.7	11.0	14.8
305	0.34	<.2	45.6	<.06	58.1	21.0	63.0
307 ^a	0.44	0.64	50.4	0.06	45.7	24.2	105.
309 ^a	0.48	0.52	90.2	0.70	53.3	12.5	35.5
311 ^a	0.46	1.95	52.2	0.06	18.3	32.9	77.6
313	0.42	<.2	37.5	0.07	43.9	25.7	81.3
315	0.55	<.2	26.9	0.07	51.9	16.3	70.8
317	0.46	<.2	31.5	0.07	50.7	15.1	56.2
319	0.30	<.2	44.2	0.42	71.4	13.2	43.7
321 ^a	0.40	0.38	46.1	0.13	58.8	13.4	10.2
323	1.07	<.2	45.7	<.06	31.4	9.2	30.9
501	0.51	1.14	21.4	<.06	55.4	13.6	148.
503	0.29	<.2	49.7	0.84	90.5	3.1	105.
505	0.18			0.76	74.0	10.6	37.2
507 ^a	0.33			0.95	51.2	14.5	19.5
509 ^a	0.54	2.37	53.7	0.52	88.1	50.9	31.6
511 ^a	0.68	0.99	53.1	0.34	171.	56.3	14.1
513 ^a	0.61	0.41	52.3	0.14	45.0	9.6	123.
515 ^a	0.66	0.36	49.3	0.08	89.1	25.9	115.
517 ^a	0.54	2.49	73.9	0.77	78.0	48.0	33.1
519 ^a	0.62	0.40	66.8	0.13	69.8	10.2	120.
521	0.26	0.47	32.2	0.06	63.3	18.2	126.
523 ^a	0.31			0.89	75.3	29.7	2.5
525	0.71	<.2	18.8	<.06	40.1	18.2	95.5
601	0.80	0.36	32.7	<.06	32.7	11.8	22.4
602 ^a	0.70	<.2	41.1	<.06	62.5	7.7	95.5
603	0.69	0.25	27.9	<.06	42.3	10.3	120.
604	0.91	0.24	27.1	<.06	35.8	18.8	81.3
605	1.14	0.69	22.4	0.12	26.5	14.6	47.9
606	1.21	0.32	21.5	0.08	31.8	17.4	81.3
607	0.74	<.2	40.7	<.06	59.1	14.1	81.3
608	0.78	<.2	22.5	<.06	21.9	8.1	120.
609	0.70	0.64	24.8	0.13	42.2	9.6	34.7
611	0.67	<.2	44.0	0.17	47.8	9.6	63.1
612	0.63	<.2	38.7	0.59	58.3	5.7	41.7
613	0.68	0.34	31.1	0.15	34.3	4.8	17.8
614 ^a	0.70	0.60		0.21	37.8	14.8	3.5
615	0.66	0.37	76.7	0.17	50.0	11.8	63.1
617	0.70	0.22	46.4	0.11	62.1	17.3	56.2
618 ^a	0.71	<.2		0.08	32.9	6.5	60.3

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 9, JULY 23, 1973
(Continued)

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
703	0.39	<.2	66.7	0.07	64.7	3.8	66.1
704	0.45	<.2	46.4	0.45	34.7	2.2	79.4
705	0.45			0.41	38.0	3.1	77.6
706	0.51			0.58	41.1	4.3	20.9
707	0.53	0.24	46.4	0.09	32.4	7.8	14.1
708 ^a	0.59	0.21	89.6	0.72	49.7	5.7	21.9
710	0.71	0.34	67.7	0.63	51.0	8.9	14.1
714	0.53	<.2	78.1	0.56	41.4	2.5	35.5
715	0.54	<.2	46.2	0.06	35.0	3.0	70.8
716	0.40	<.2	51.0	0.17	50.2	2.5	77.6

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 10, JULY 23, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
007	1.62	<.2	60.0	0.09	31.4	29.6	79.4
009 ^a	1.57	0.98	34.0	0.29	11.7	25.5	6.9
010	b	0.31	38.3	0.19	25.1	29.8	5.4
011	1.62	<.2	41.5	0.08	17.8	24.2	43.7
012	b	<.2	18.9	0.07	16.0	21.6	41.7
013	1.46	<.2	24.5	<.06	28.1	21.6	38.0
014	b	<.2	20.0	0.08	13.0	22.5	58.9
016	1.54	<.2	9.7	<.06	9.9	13.9	35.5
017	1.56	0.22	16.1	<.06	10.8	11.6	17.8
018	1.52	<.2	20.3	<.06	18.7	23.3	25.1
019	1.47	<.2	36.0	<.06	25.0	28.3	102.
020	1.49	<.2	24.5	<.06	26.9	20.1	64.6
120	2.7	<.1	27.4	<.06	6.9	7.3	38.9
104	2.0	<.1	27.2	<.06	7.2	9.8	61.7
106	1.51	<.1	29.1	<.06	13.3	14.0	83.2
108	3.1	<.1	45.7	<.06	19.0	21.2	105.
110	2.4	<.1	67.2	<.06	16.7	9.8	151.
112	1.56	<.1	42.4	<.06	19.9	17.1	123.
114	3.8	<.1	32.2	<.06	16.1	22.0	87.1
116	3.1	<.1	48.8	<.06	26.1	22.3	105.
118	2.4	<.1	53.6	<.06	27.0	19.9	
120	0.97	<.1	59.8	<.06	24.9	15.8	186.
122	2.0	<.1	41.6	<.06	24.0	20.2	102.
124	2.4	<.1	31.2	<.06	20.3	10.5	57.5
201	b	<.1	28.4	<.06	2.4	14.3	46.8
203		<.1		<.06	10.4	15.1	126.
205	0.64	<.1	86.7	<.06	46.3	18.1	117.
207	0.37	<.1	99.7	0.10	60.9	21.8	97.7
209	0.16	<.1	209.	0.11	21.4	12.8	50.1
211	0.61	<.1	56.6	0.07	34.9	42.8	77.6
213 ^a	0.50	<.1	108.	0.07	52.7	26.3	120.
215 ^a	1.15	<.1	44.7	<.06	19.6	16.3	112.
217	1.50	<.1	57.6	<.06	41.5	24.1	120.
219 ^a	0.55	<.1	90.2	0.08	32.2	31.9	132.
221 ^a	1.54	<.1	40.8	<.06	30.5	15.1	89.1
223	1.34	<.1	38.6	<.06	20.3	18.1	93.3
225	b	<.1	26.0	0.08	26.1	13.2	37.2

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 10, JULY 23, 1973. (Continued)

Sample Position	Rainfall cm	Concentration (gm-moles/l) $\times 10^6$					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
301	1.53	1.52	88.4	0.73	47.1	29.2	38.9
303	1.28	<.2	94.0	0.13	55.5	32.5	102.
305	1.09	<.2	52.6	0.07	77.4	21.5	129.
307	0.63		50.0	<.06	24.8	35.8	123.
315	0.15	0.32	32.1	<.06	36.1	18.4	51.3
319	0.45	0.22		0.06	47.9	16.7	132.
321	0.69	0.24	65.5	0.14	31.6	19.9	224.
323	1.51		83.3	<.06	27.7	19.3	75.9
501	0.87	<.2		0.06		13.1	112.
503	0.19						112.
505	0.16	<.2	30.8	<.06	42.5	16.5	75.9
507	0.17	0.38	61.1		55.1	46.9	56.2
523	0.17	<.2	18.4	0.08	39.2	21.6	69.2
525	0.25	<.2	24.5	0.08	31.8	22.6	77.6
601 ^a	0.43		71.9	0.07	42.2	18.8	250.
602	0.63		65.6	<.06	35.0	16.9	288.
603	0.37		50.4	0.12	13.8	11.0	145.
604	1.24	0.24	67.1	<.06	31.6	16.0	191.
605	0.49		60.4	0.07	30.1	20.4	158.
606	0.37		41.0	<.06	32.5	17.4	178.
607	0.52		30.2	<.06	30.8	18.6	151.
615	1.16	<.2	107.	0.07	23.2	19.3	77.6
701	b		22.9	0.07	7.2	16.0	37.2
702	b		30.2	<.06	15.5	8.3	20.9
703	2.6		15.7	0.12	8.9	9.9	39.8
704	2.6		35.4	<.06	12.5	13.5	38.9
705	1.40		59.4	0.06	20.4	15.3	100.
708	1.8		62.5	<.06	23.8	23.3	95.5
710	1.48		74.0	0.09	26.5	23.5	20.0
711	0.91		67.7	<.06	31.6	20.0	126.
713	2.7		80.2	0.07	15.9	21.9	12.3
714	b		43.8	<.06	12.2	14.2	57.5
715	b		27.1	<.06	8.0	10.1	47.9
716	b		21.9	<.06	8.5	9.4	26.3

^aQuestionable quality - see text.

^bSampler overflowed. Will be estimated later from raingage records.

SEQUENTIAL SAMPLE CONCENTRATIONS OF INORGANIC,
NONMETALLIC POLLUTANTS - RUN 10, JULY 23, 1973.

Sample Position (Sequential)	Rainfall Rate cm/hr	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
301-O	2.15	<.1	95.8	0.07	29.8	36.8	126.
P	0.57	<.1	144.	0.07	49.0	68.0	20.4
Q	2.66	<.1	99.0	0.07	30.5	41.7	117.
R	1.54	<.1	70.8	0.07	27.2	26.7	141.
S	2.81	<.1	97.9	.06	28.3	24.0	158.
T	0.93	<.1	115.	.06	35.3	29.6	204.
U	0.12	<.1	144.	.06	49.3	44.1	407.
V	0.31	<.1	148.	0.10	80.1	45.9	407.

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 11, JULY 24, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
303	1.59	0.22	72.6	0.06	50.8	30.8	123.
305	0.53	<.2	62.4	.06	50.6	23.7	178.
707	0.27	<.2	135.	0.20	162.	66.8	158.
708	1.56	<.2	92.0	0.10	77.8	52.2	178.

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 12, JULY 25, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
317	0.12		91.0		52.8	14.9	79.4
319	0.40	<.1	60.4	<.06	44.9	9.3	155.
321	0.25	0.26	101.	0.08	58.7	18.5	49.0
405	0.16		105.		72.2	11.6	41.7
419	0.16		40.6		34.6	36.7	51.3
427	0.27	0.61	96.5	0.13	47.3	12.9	3.5
509	0.67	<.1	20.7	0.10	19.0	24.2	60.3
511	0.38	<.1	38.8	<.06	20.9	12.9	93.3
513	0.23	<.1	73.2		36.1	11.8	151.
515	0.19		64.4		28.3	12.4	120.
517	0.13		109.		45.7	16.7	16.6
519	0.62	<.1	18.3	<.06	15.9	16.4	89.1
521	0.19		35.8		32.4	55.1	66.1
606 ^a	0.62	<.1	106.	<.06	49.6	17.0	151.

CONCENTRATIONS OF INORGANIC, NONMETALLIC
POLLUTANTS - RUN 13, JULY 25, 1973.

Sample Position (Sequential)	Rainfall Rate cm/hr	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
200-A	1.07	3.25	68.8	<.06	30.3	24.3	126.
B	0.26	2.46	58.3		29.1	5.5	245.
C	0.24	4.52	26.0	<.06	14.7	5.3	126.
D	0.80	2.24	83.3	<.06	24.7	9.5	162.
E	0.73	3.19	41.7	<.06	12.2	4.6	132.
F	0.26	3.88	36.5	<.06	10.4	3.6	120.
G	0.30	1.74		<.06	13.0	6.0	126.
H	0.37	4.28	36.5	<.06	6.7	1.2	95.5

CONCENTRATIONS OF INORGANIC NONMETALLIC
POLLUTANTS - RUN 14, JULY 25-26, 1973.

Sample Position	Rainfall cm	Concentration (gm-moles/l) $\times 10^6$					
		SO ₂	SO ₄ ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
007	0.44	<.2	24.5	0.06	17.3	14.0	25.7
008	0.21	0.99	46.8	0.07	33.0	21.8	1.4
010 ^a	0.20	<.2	29.2	<.06	21.2	15.7	38.0
011	0.23	0.21	38.5	0.19	23.1	14.5	3.9
012	0.37	<.2	23.0	0.06	8.2	8.2	19.1
013	0.57	<.2		0.07	9.0	8.2	35.5
014	0.85	0.56	47.9	0.07	21.0	8.5	46.8
015	1.33	0.24	29.5	<.06	15.0	7.2	40.7
016	b	0.35	14.7	<.06	5.1	5.5	31.6
017	b	<.2	12.5	<.06	5.5	7.7	30.9
018	b	<.2		<.06		5.1	19.5
019	1.18	<.2	27.1	<.06	4.5	7.5	28.2
020	1.34	<.2	13.5	<.06	4.5	7.7	38.9
022	0.68	<.2	18.8	<.06	7.6	9.0	9.5
102 ^a	b	<.2	43.6	<.06	14.8	10.8	51.3
104 ^a	b	<.2	27.1	<.06	10.5	8.0	57.5
106 ^a	b	0.30	73.0	<.06	25.3	16.5	174.
108 ^a	1.55	0.78	55.2	0.13	42.6	26.5	251.
110 ^a	0.81	1.09	89.4	0.10	79.1	29.9	64.6
112 ^a	1.04	0.48	83.3	0.10	75.7	26.3	324.
114 ^a	b	<.2	63.5	0.06	54.1	18.6	389.
116 ^a	0.88	0.82	64.9	0.06	35.3	18.6	158.
118 ^a	1.36	0.26	95.8	0.06	53.3	19.1	355.
124 ^a	1.18	0.31	57.3	0.11	35.5	14.5	120.
201	0.20		73.7	0.52	29.1	11.4	5.6
205	0.31	0.82	75.3	0.10	30.7	15.0	66.1
209	0.53	0.55	67.5	<.06	38.5	22.4	75.9
213	0.57	0.78	63.3	<.06	44.9	29.1	112.
215	1.26	1.07	45.7	0.14	28.8	15.2	100.
217	0.51	0.26	59.2	0.07	28.9	13.7	126.
223	0.62	0.31	51.8	<.06	28.2	11.0	141.
225	1.30	<.2	64.5	<.06	24.9	11.0	186.
309	0.43	0.29	80.1	<.06	31.6	29.3	162.
311		<.2	22.7	<.06	10.8	9.0	126.
313	0.87	<.2	32.8	<.06	21.8	17.2	112.
315	0.57	0.26	47.5	<.06	26.1	25.9	52.5
317	1.00	<.2	35.5	<.06	15.3	15.2	97.7

CONCENTRATIONS OF INORGANIC NONMETALLIC
POLLUTANTS - RUN 14, JULY 25-26, 1973.
(Continued)

Sample Position	Rainfall cm	Concentration (gm-moles/l) x 10 ⁶					
		SO ₂	SO ₄ ⁼	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
601	0.11		40.6		19.5	15.7	38.0
602	0.07		47.9				55.0
603	0.12		46.9				36.3
604	0.16	<.2		0.07			57.5
605 ^a	0.17		31.3		32.8	12.7	23.4
607 ^a	0.29	<.2	28.1	0.07	16.1	18.3	46.8
608	0.25	<.2		0.07		15.0	83.2
609	0.18		26.0	0.09	17.1	13.4	69.2
610	0.16		28.1		22.6	14.5	0.5
611	0.16		25.0		24.7	6.0	15.5
618	0.31	<.2	63.5	0.30	20.6	18.8	7.1
701	b	0.30	28.1	<.06	13.4	9.5	44.7
702	1.17	4.71	35.9	0.10	18.8	12.9	97.7
703	0.80	1.75	53.3	<.06	22.9	14.0	93.3
704	0.71	0.43	59.5	<.06	27.2	16.4	95.5
705	0.43	0.21	57.2	<.06	55.3	14.8	29.5
706	0.26		50.2	0.10	22.8	10.0	3.2
707	0.12		92.8		30.0	19.2	1.0
708	0.11		136.		45.8	21.7	1.0
714	0.56	1.25	61.8	<.06	29.8	11.8	25.1
715	0.84	.18	44.2	<.06	20.9	12.3	87.1
716	1.14	0.89	60.6	0.10	26.7	9.6	112.

^aQuestionable quality - see text.

^bSampler overflowed. Will be estimated later from raingage records.

does not harm the measurements for all but SO_2 . Thus the overnight samples may be more useful than we had thought earlier. Some changes in concentration appear to occur with time, but these at present do not seem to be in any particular pattern or due to any recognized cause.

Aircraft Sampling

Through cooperation with concurrent field activities, we were able to collect significant airborne measurements of pollutants. Approximately half the field time period was allocated for pollutant gas and particle size distribution measurements, and the other half for tracer releases for the AEC-sponsored METROMEX Tracer Scavenging program. Unfortunately, the former period was characterized by fair weather, so our measurements did not directly relate to precipitation-sampled storms. During the latter period, on non-storm days, high-volume air samples were taken. These will be analyzed for inorganic pollutant content.

The most notable achievement of the aircraft sampling in support of this project was the successful aircraft operation of a chemiluminescent NO-NO_x monitor. Vertical profiles of NO-NO_x content were flown on several occasions, upwind, downwind, and over the city. These were timed for close coordination with ground-level measurements using the same type of instrument. These latter were done by researchers of Battelle, Columbus, who were based at St. Louis University in downtown St. Louis. The data are in the process of analysis and interpretation, but it has been found that the concentrations of both NO_x and NO at 1500 ft MSL were higher than those at the ground. The nitrogen oxides levels then decreased with height above 1500 feet.

APPENDIX B: SOME REFERENCES PERTINENT TO THE FIELD
OF PRECIPITATION CHEMISTRY

As noted in Table 2, virtually no direct information is available regarding airborne chemical transformations significant to scavenging within the St. Louis field-experiment system. Because of the embryonic state of knowledge of this subject, we have compiled a brief review of precipitation chemistry to provide some basis for practical application and further research in the field.

The references included here are by no means a complete listing of articles covering all aspects of precipitation chemistry. Notably missing, for instance, is the significant number of articles pertaining to contributions in the areas of biological and surface response. These have been omitted for brevity and because they have only an indirect relationship with the atmospheric removal and transformation processes of primary concern in this work.

Early portions of the reference listing are itemized according to positions of specific elements on the periodic chart. Other more general categories are included in the later portions to contain multiple categories (metals, nonmetallic inorganics, organics, inorganics, and "general"). Articles within each category are listed in alphabetical order of the names of the first authors.

GROUP I - Elements H, Li, Na, K, Rb, Cs

1. Barrett, E. and G. Brodin. The Acidity of Scandinavian Precipitation. *Tellus*. 7:251-257, 1955.
2. Hogan, Austin W. and T. A. Rich. Mobile Tracing Technique Utilizing a Meteorologically Inert Lithium Aerosol. *Atmos. Sci. Res. Center*. State University of New York, Albany, N.Y.
3. Likens, G. E. and F. H. Bormann and N. M. Johnson. Acid Rain. *Environment*. 14:33-40, 1972.
4. Moghissi, A. Alan, and Charles R. Porter. Tritium Concentration in Precipitation. *Radiol. Health Data Rep*. 11:137-40, 1970.

5. Nyberg, Alf. Weather Changes Important for the Acidity of Rainfall. *Forsk. Framsteg.* 1:18-21, 1970.
6. Warburton, J. A. and L. G. Young. Neutron Activation Measurements of Silver in Precipitation from Locations in Western North America. *J. Appl. Meteorol.* 7:444-448, 1968.

GROUP II - Elements Be, Mg, Ca, Zn, Sr, Cd, Ba, Hg, Ra

GROUP III - Elements B, Al, Sc, Ga, Y, In

GROUP IV - Elements C, Si, Ti, Ge, Zr, Sn, Hf, Pb

1. Atkins, Patrick R. Lead in a Suburban Environment. *J. Air Pollut. Contr. Assoc.* 19:591-594, 1969.
2. Francis, Chester W., Gordon Chesters, and Larry A. Haskin. Determination of Lead-210--Mean Residence Time. *Environ. Sci. Technol.* 4:586-589, 1970.
3. Galbally, I. E. Production of Carbon Monoxide in Rainwater. *J. Geophys. Res.* 77:7129-7132, 1972.
4. Lazrus, Allan L., Elizabeth Lorange, and James P. Lodge, Jr. Lead and Other Metal Ions in United States Precipitation. *Environ. Sci. Technol.* 4:55-58, 1970.
5. Preobrazhenskaya, E. V. Measurements of the Lead Concentration in Rainfall During its Natural Fallout and During the Action of Lead Iodide on the Clouds. *Tr. Gl. Geofiz. Observ.* 239:43-48, 1969.

GROUP V - Elements N, P, V, As, Cb, Sb, Ta, Bi

1. Angström, A. and L. Högberg. On the Content of Nitrogen in Atmospheric Precipitation. *Tellus.* 4:31-42, 1952.
2. Burtsev, I. I., L. V. Bertseva, and S. G. Malakhov. Washout Characteristics of Phosphorus-32 Aerosols Injected into Clouds. *Issled. Protsesov Samoochishcheniya Atmos. Radioaktiv. Izotop. Sb. Dokl., Soveshch.* 335-345, 1966. Pub. 1968.
3. Commoner, Barry. Threats to the Integrity of the Nitrogen Cycle. Nitrogen Compounds in Soil, Water, Atmosphere, and Precipitation. *Global Eff. Environ. Pollut. Symp.* 70-95, 1968, Pub. 1970.
4. Drover, D. P. and I. P. Barrett-Lennard. Accessions of Nitrogen in Western Australian Wheat Belt Rains. *J. Aust. Agric. Sci.* 22:193-197, 1956.

5. Eriksson, E. Composition of Atmospheric Precipitation I. Nitrogen Compounds. *Tellus*. 4:215-233, 1952.
6. Gosz, James R. Sources of Nitrogen in Precipitation and Sedimentation Near Moscow, Idaho. Avail. University Microfilms, Ann Arbor, Mich. Order No. 70-10, 701. 85 p. 1969. From Diss. Abstr. Int. B 1970. 30(12) Pt. 1, 5312.
7. Jones, M. J. Ammonium and Nitrate Nitrogen in the Rainwater at Samaru, Nigeria. *Tellus*. 23: 459-461, 1971.
8. Junge, C. E. The Distribution of Ammonia and Nitrate in Rainwater Over the United States. *Trans. A.G.U.* 39:241-248, 1958.
9. Lavrinenko, R. F. Amount of Nitrogen Compounds in Precipitation During Storms. *Tr. Gl. Geofiz. Observ. (Russ)* No. 234, 205-207, 1968.
10. McConnell, J. C. Atmospheric Ammonia. *J. Geophys. Res.* 78:7812-7821, 1973.
11. Meyer, J. and E. Pampher. Nitrogen Content of Rainwater Collected in the Humid Central Congo Region. *Nature*. 184:717-718, 1959.
12. Nucciotti, F. and N. Rossi. Chemical Composition of Atmospheric Precipitation in Emilia II. Nitrous, nitric, and ammoniacal nitrogen and phosphorus. *Agrochimica*. 12:536-544, 1968. (Ital.)
13. Popovsky, Jiri. Phosphorus, Arsenic, and Germanium Compounds in Rain Water. *Vod. Hospod.* 18:24-26, 1968. (Czech.)
14. Reiter, R. Further Experimental Evidence for the Importance, With Respect to Thunderstorm Electrification, of Nitrate Ions Contained in Precipitation. II. *J. Atmos. Terr. Phys.* 30:345-362, 1968.
15. Scharrer, K. and H. Fast. Investigations of Plant Nutrients Supplied to Soil in Precipitation. *A. Pflernähr. Düng.* 55:97-106, 1951.
16. Shilina, L. I. Introduction of Nitrogen into Soils by Means of Atmospheric Precipitation and Its Extraction with Lysimetric Water. *Zemlerobstvo, Respub. Mizhvidom. Temat. Nauk. Zb.* 2:102-106, 1967.
17. Syers, J. K. The Relationship Between the Concentration of Nitrate and Ammonia Nitrogen in Precipitation. *Tellus*. 28:146-147, 1966.
18. Tarrant, R. F., K. C. Lu, C. S. Chen, and W. B. Bollen. Nitrogen Content of Precipitation in a Coastal Oregon Forest Opening. *Tellus*. 20:554-556, 1968.

19. Tsunogai, Shizuo. Ammonia in the Oceanic Atmosphere and the Cycle of Nitrogen Compounds Through the Atmosphere and Hydrosphere. *Geochem. J.* 5:57-67, 1971.
20. Viemeister, P. E. Lightning and the Origin of Nitrates Found in Precipitation. *J. Meteorol.* 17:68,-683, 1960.
21. Virtanen, A. J. Molecular Nitrogen Fixation and Nitrogen Cycle in Nature. *Tellus.* 4:304-306, 1952.
22. Weinmann, H. The Nitrogen Content of Rainwater in Southern Rhodesia. *S. Afr. J. Sci.* 52:82-84, 1955.
23. Wetselaar, R. and J. T. Hutton. The Ionic Composition of Rainwater at Katherine, N. T. and Its Part in the Cycling of Plant Nutrients. *Aust. J. Agr. Res.* 14:319-329, 1963.
24. Yaalon, D. H. The Concentration of Ammonia and Nitrate in Rainwater Over Israel in Relation to Environmental Factors. *Tellus.* 16:200-204, 1964.

GROUP VI - Elements O, S, Cr, Se, Mo, Te, W, Po

1. Barrow, N. J., Keith Spencer, and W. M. McArthur. Effects of Rainfall and Parent Material on the Ability of Soils to Adsorb Sulfate. *Soil Sci.* 108:120-126, 1969.
2. Bassett, H. and W. G. Parker. Oxidation of Sulfurous Acid. *J. Chem. Soc.* 1540-1560, 1951.
3. Beilke, S. and H. Georgii. Investigation on the Incorporation of Sulfur Dioxide into Fog and Rain Droplets. *Tellus.* 20:435-441, 1967.
4. Beilke, S., D. Lamb, and J. Miller. Neue Untersuchungen zur Oxidation von Schwefeldioxid in Gegenwart von Flüssigwasser. Report, Universität-Institute für Meteorologie und Geophysik, Frankfurt/Main, Germany.
5. Cheng, R. T., M. Corn, and J. O. Frohlinger. Contribution to the Reaction Kinetics of Water Soluble Aerosols and SO₂ in Air at PPM Concentrations. *Atm. Env.* 5:987-1008, 1971.
6. Cortecchi, G. and Antonio Longinelli. Isotopic Composition of Sulfate in Rain Water, Pisa, Italy. *Earth Planet Sci. Lett.* 8:36-40, 1970.
7. Dana, M. Terry, J. M. Hales, and M. A. Wolf. Natural Precipitation Washout of Sulfur Compounds from Plumes. Final Report to the Environmental Protection Agency, Raleigh, NC. Publication No. R3-73-047. 1973. 202 p.

8. Eriksson, E. The Yearly Circulation of Sulfur in Nature. Jour. Geophys. Res. 68:4001-4008, 1963.
9. Fuller, E. C. and R. H. Christ. The Rate of Oxidation of Sulfite Ions by Oxygen. J. Am. Chem. Soc. 63:1644-1650, 1941.
10. Gallagher, P. A. Effect of Sulfur in Fertilizers, Rainwater, and Aoiila on Crop Nutrition. Sci. Proc. Roy. Dublin Soc., Ser. B 2: 191-204, 1969.
11. Georgii, H. W., Contribution to the Atmospheric Sulfur Budget. J. Geoph. Res. 75:2365-2371, 1970.
12. Georgii, H. W. On the Effect of Rainfall on the SO₂ Concentration in the Atmosphere. Int. J. Air Wat. Poll. 7:1057-1059, 1963.
13. Gerhard, E. R. and H. F. Johnstone. The Photochemical Oxidation of Sulfur Dioxide to Sulfur Trioxide and Its Effect on Fog Formation. Ind. Eng. Chem. 47:972-976, 1965.
14. Granat, L. and H. Rodhe. A Study of Fallout by Precipitation Around an Oil Fired Power Plant. Atmos. Env. 7, 781-792, 1973.
15. Hales, J. M. and S. L. Sutter. Solubility of Sulfur Dioxide in Water at Low Concentrations. Atm. Envi. 7:997-1001, 1973.
16. Hales, J. M., J. M. Thorp, and M. A. Wolf. Field Investigation of Sulfur Dioxide Washout from the Plume of a Large Coal-Fired Power Plant. Final Report to Environmental Protection Agency. Publication Number BNW-389, 1971.
17. Hanley, P. K. and S. L. Tierney. Sulfur Studies. I. Contribution of Sulfur in Precipitation to Crop Production in Ireland. Irish J. Agr. Res. 8:19-27, 1969.
18. Hashimoto, Yoshikazu and John W. Winchester. Selenium in the Atmosphere. Environ. Sci. Technol. 1:338-340, 1967.
19. Hoather, R. C. and C. F. Goodeve. The Oxidation of Sulfurous Acid. Trans. Far. Soc. 30:1149-1156, 1934.
20. Hutcheson, M. R. and F. P. Hall. Sulfate Washout from a Coal-Fired Power Plant Plume. Atm. Envi. (in Press).
21. Johnstone, H. F. and D. R. Coughanowr. Absorption of Sulfur Dioxide from Air. I and E.C. 50:1169, 1958.
22. Johnstone, H. F. and A. J. Moll. Formation of Sulfuric Acid in Fogs. I and E.C. 52:861, 1960.

23. Junge, C. E. Sulfur in the Atmosphere. *J. Geoph. Res.* 65:227-237, 1960.
24. Junge, C. E. and T. G. Ryan. The Oxidation of Sulfur Dioxide in Dilute Solutions. *Quart. J. Roy. Met. Soc.* 84:46-55, 1958.
25. Lavrinenko, R. F. Sulfur Content in Rainfall. *Tr. Gl. Geofiz. Observ.* 207:87-91, 1968.
26. Matteson, M. J., W. Stueber, and H. Luther. Kinetics of the Oxidation of Sulfur Dioxide by Aerosols of Manganese Sulfate. I and E.C. *Fund* 8:677-687, 1969.
27. McKay, H. A. The Oxidation of Sulphur Dioxide in Water Droplets in the Presence of Ammonia. *Atm. Envi.* 5:7-14, 1971.
28. Miller, J. M. A Model for the Rainout and Washout of Sulfates in the Atmosphere. Penn. State University Center for Air Environment Studies Pub. No. 239-72, 1972.
29. Miller, J. M. and R. G. dePena. Contribution of Scavenged Sulfur Dioxide to the Sulfate Content of Rainwater. *J. Geophys. Res.* 77:5905-5916, 1972.
30. Miller, J. M. and R. G. dePena. The Rate of Sulfate Ion Formation in Water Droplets in Atmospheres with Different Partial Pressures of SO_2 . In: *Proc. 2nd Int. Clean Air Congress, Washington, DC, Dec. 6-11, 1970.*
31. Mizutani, Yoshihiko, and T. Atho Rafter. Oxygen Isotopic Composition of Sulfates. V. Isotopic Composition of Sulfate in Rain Water, Gracefield, New Zealand. *N. Z. J. Sci.* 12:69-80, 1969.
32. Penkett, S. A. Oxidation of SO_2 and Other Atmospheric Gases by Ozone in Aqueous Solution. *Nature Phys. Sci.* 240:55-106, 1972.
33. Rodhe, Henning. Residence Time of Anthropogenic Sulfur in the Atmosphere. *Tellus.* 22:137-139, 1970.
34. Rodhe, Henning. A Study of the Sulfur Budget Over Northern Europe. *Tellus.* 24:128-135, 1972
35. Rodhe, Henning. A Study of the Sulfur Budget for the Atmosphere Over Northern Europe. Final Report AC-17 International Meteorological Institute (Stockholm). 1971.
36. Scott, W. D. and P. V. Hobbs. The Formation of Sulfate in Water Droplets. *J. Atmos. Sci.* 24:54-57, 1967.

37. Shaw, R. W. and D. M. Welpdale. Sulfate Deposition by Precipitation in Lake Ontario. *Water, Air, Soil Pollut.* 2:125-128, 1973.
38. Summers, P. W. Scavenging of SO₂ by Convective Storms. In: *Precipitation Scavenging.* USAEC Conf 700601, 1970.
39. Sweden's Case Study Contribution to the United Nations Conference on the Human Environment. Royal Ministry of Foreign Affairs, Royal Ministry of Agriculture, 1971.
40. Val'nikov, I. U. Amount of Sulfur Depositing on the Earth's Surface with the Atmospheric Precipitation in Tatar SSR. *Biol. Nauki.* 14:110-111, 1971.
41. Val'nikov, I. U. Sulfur Turnover and Its Importance for Crop Production in Tatar ASSR. *Pochvovedenie.* 3:40-47, 1971.
42. Van Den Heuvel, A. P. and B. J. Mason. The Formation of Ammonium Sulfate in Water Droplets Exposed to Gaseous Sulfur Dioxide and Ammonia. *Q. J. Roy. Met. Soc.* 89:271-275, 1963.
43. Walker, D. R. Sulfur in Precipitation in Central Alberta. *Can. J. Soil Sci.* 49:409-410, 1969.
44. Witt, Ernst. Lethal Effect of Exhaust Gases on the Water Fauna. *Zentralbl. Arbeitsmed. Arbeitsschutz.* 19:264-265, 1969.

GROUP VII - Elements F, Cl, Mn, Br, Te, I, Re, At

1. Chamberlain, A. C. and R. C. Chadwick. Transport of Iodine from Atmosphere to Ground. *Tellus.* 18:226-237, 1966.
2. Duce, Robert A., John W. Winchester, and Theodore W. van Nahl. Iodine, Bromine, and Chlorine in Winter Aerosols and Snow From Barrow, Alaska. *Tellus.* 18:238-248, 1966.
3. Garber, Kurt. Fluoride in Rain Water and Vegetation. *Fluoride Quart. Rep.* 3:22-26, 1970.
4. Harriss, Robert C. and Harold H. Williams. Specific-ion Electrode Measurements on Bromine, Chlorine, and Fluorine in Atmospheric Precipitation. *J. Appl. Meteorol.* 8:299-301, 1969.
5. Inoue, Tomoo and Jishin Kobayashi. Distribution of Chloride in Rain Water and Land Forms in the Northern Tohoku District. *Shigen Kagaku Kenkyusho Iho.* 75:73-80, 1971.
6. Shmeter, S. M. On the Content of Chloride in Cloud Water in Connection with Fine-Scale Structure. *Trudy ZAO.* 9, 1952.

7. Svistov, P. F. and E. S. Selezneva. Some Data on Chemical Composition and Distribution of Aerosols on the Kola Peninsula Coast. Tr. Gl. Geofiz. Observ. 185:116-116, 1966. (Russ)
8. Valach, R. The Origin of the Gaseous Form of Natural Atmospheric Chlorine. Tellus. 19:509-516, 1967.
9. Valach, Roman. Fluoride and Chloride in Precipitation of Bohemia. Stud. Geophys. Geod. Cesk. Akad. Ved. 11:241-251, 1967.
10. Zerche, M. and W. Haensch. Determination of the Chloride Content of Precipitation in the Schwerin/Mecklenburg Area. Z. Meteorol. 19:97-101, 1967.

GROUP VIII - Elements Fe, Co, Ru, Rh, Os, Ir

GROUP O - Noble Gases

1. Loosli, H. H., Hans Oeschger, and W. Wiest. Argon-37, Argon-39, and Krypton-81 in the Atmosphere and Tracer Studies Based on These Isotopes. J. Geophys. Res. 75:2895-2900, 1970.

METALS

1. Belyaev, L. I. and E. I. Ovsyanyi. Trace Elements in Atmospheric Precipitation in a Coastal Region in Relation to Some Problems of Chemical Oceanography. Gidrokhim. Mater. 51:3-12, 1969. (Russ).
2. Bogdanova, L. L. Role of the Composition of Atmospheric Precipitation in the Formation of Fracture Waters in Weathering Profiles of the Transbaikalia Mountain Structures. Form. Geokhim. Podzemn. Vod Sib. Dal'nego Vostoka. Inst. Zemnoi Kory Sib. Otd. Akad. Nauk SSSR 64-73, 1967. (Russ)
3. Drozdova, V. M. and E. P. Makhon'ko. Content of Trace Elements in Precipitation. J. Geophys. Res. 75:3610-3612, 1970.
4. Drozdova, V. M. and P. F. Svistov. Trace Element Content in Rainfall. Tr. Gl. Geofiz. Observ. 207:92-97, 1968. (Russ)
5. Garber, Kurt. Air Pollution by Heavy-Metal-Containing Dusts. Effects on Plants. Landwirt. Forsch. Sonderh. 25:59-68, 1970. (Ger)
6. Hanappe, F., M. Vosters, E. Picciotto, and S. Deutsch. Chemistry of Antarctic Snows and Deposition Rate of Extraterrestrial Matter. II. Earth Planet Sci. Lett. 4:487-496, 1968.

7. Lag, J. General Problems in Soil Chemistry in Relation to the Chemical Composition of the Precipitation. Medlemsbl. Nor. Veterinaerforen. 21:117-124, 1969. (Norweg)
8. Lazrus, A. L., E. Lorange, and J. P. Lodge. Lead and Other Metal Ions in United States Precipitation. Env. Sci. Tech. 4:55-57, 1970.
9. Makhon'ko, E. P. and V. M. Drozdova. Trace Element Level in Precipitation. Tr. Inst. Eksp. Meteorol. 14:81-85, 1971. (Russ)
10. Ragone, S. E. and C. A. Wolf. Analysis of the Major Cationic Constituents of Dye Sites 2 and 3, Greenland. U. S. Nat. Techn. Inform. Service. AD Rep. No. 743473, 1972. 13 p.
11. Steffe, Dirl H. Control of Contamination in Hail Samples Collected for Trace Metal Analysis. J. Appl. Meteorol. 9:193-194, 1970.
12. Von Arx, U., V. Zeier, and M. Semlitsch. Microstructure Studies on Magnetic Spheroids Found in Alpine Snow and Foundry Dust Samples in Switzerland. Sulzer Tech. Rev. 52:268-274, 1970.

NONMETALLIC INORGANICS

1. Beilke, S. Research Concerning the Washout of Precipitation of Atmospheric Elements. University of Frankfurt/Main, Germany. Report APTIC TR-0701, 1970.
2. Eriksson, E. The Yearly Circulation of Chloride and Sulfur in the Atmosphere, Part I. Tellus. 11:375-403, 1959.
3. Eriksson, E. The Yearly Circulation of Chloride and Sulfur in Nature, Part II. Tellus. 11:375-403, 1959.
4. Garland, J. A., J. R. Branson, and L. C. Cox. Study of the Contribution of Pollution to Visibility in a Radiation Fog. Atm. Env. 7:1079-1092, 1973.
5. Georgii, Hans W. Untersuchungen Über Atmosphärische Spurenstoffe Und Ihre Bedeutung Für Die Chemie der Niederschläge. Geofisica Pura E Applicata. Bd. 47:155-171, 1960.
6. Georgii, Hans W. and Dieter Woetzel. Relation Between Drop Size and Concentration of Trace Elements in Rain Water. J. Geophys. Res. 75:1727-1731, 1970.
7. Hoeft, R. G., D. R. Keeney, and L. M. Walsh. Nitrogen and Sulfur in Precipitation and Sulfur Dioxide in the Atmosphere in Wisconsin. J. Environ. Qual. 1:203-208, 1972.

8. Houghton, H. C. The Chemical Composition of Fog and Cloud Water. *Journ. of Meteorology*. 12:355-357, 1955.
9. Leland, E. W. Nitrogen and Sulfur in the Precipitation at Ithica, N. Y. *Agron. J.* 44:172-175, 1952.
10. Ludwig, F. L. and E. Robinson. Observation of Aerosols and Droplets in California Stratus. *Tellus*. 23:163-170, 1971.
11. Mrose, H. Measurements of pH and Chemical Analyses of Rain-, Snow-, and Fog-water. *Tellus*. 18:266-270, 1969.
12. Piskunov, L. I. Background and Anomalous Correlations of Chlorides and Sulfates in Atmospheric Precipitation. *Dokl. Akad. Nauk SSSR* 193:1388-1391, 1971. (Russ)

ORGANICS

1. Atkins, D. H. F., and A. E. J. Eggleton. Studies of Atmospheric Washout and Deposition of γ -BHC [γ -benzene hexachloride], Dieldrin, and pp-DDT Using Radiolabeled Pesticides. *Nucl. Tech. Environ. Pollut. Proc. Symp.* 521-523, 1970.
2. Bakhanova, R. A., and E. G. Solyanek. Application of Surface-Active Agents to Prevent Water Evaporation Fogs Over the Nonfreezing Water Basins in Winter. *Proc. Int. Conf. Cloud Phys.* 688-693, 1968.
3. Bakhanova, R. A., E. G. Solyanek and F. S. Terziev. Method for Producing Films of Surfactants from Highly Dispersed Aqueous Suspensions of Higher Aliphatic Alcohols for Modifying the Vaporization Fog. *Tr. Vses. Konf. Fiz. Oblakov Aktiv. Vozdeistviyam*, 8th. 319-324, 1969. (Russ)
4. Gernet, E. V., S. M. Gliklikh, M. N. Koshta and V. A. Fedoseev. Feasibility of Fog Stabilization Using Surfactants. *Mezhvuz. Konf. Vop. Ispareniya, Goreniya Gazov. Din. Dispersynykh Sist., Mater.*, 6th 4-9, 1966. (Publ. 1968, Russ)
5. Kuehne, Rudolf, Helmut Diery, and Siegbert Rittner. Fog-Eliminating Agents. *Ger. Offen.* 2,016,705 28 Oct 1971, Appl. 08 Apr. 1970; 11 p.
6. Parker, Bruce C. Rain as a Source of Vitamin B₁₂. *Nature*. 219:617-618, 1968.
7. Semenov, A. D., L. I. Nemtsefa, T. S. Kishkinova and A. P. Pashanova. Organic Substances of Atmospheric Precipitations. *Dokl. Akad. Nauk SSSR*. 173:1185-1187, 1967. (Russ)

8. Semenov, A. D. and T. S. Kishkinova. Carbonyl Compounds in Natural Waters. *Gidrokhim. Mater.* 44:83-87, 1968. (Russ)
9. Sidle, Alan B. Amino Acid Content of Atmospheric Precipitation. *Tellus.* 19:128-135, 1967.
10. Skopintsev, B. A., A. J. Bakulina and N. I. Mel'nikova. Total Organic Carbon in Atmospheric Precipitations. *Gidrokhim. Mater.* 16:3-10, 1971.
11. Tarrant, K. R. and J. O'G. Tatton. Organochlorine Pesticides in Rainwater in the British Isles. *Nature.* 219:725-727, 1968.

INORGANICS

1. Agarwal, V. . and G. P. Roy. Note on Plant Nutrients in Rainwater at Varanasi. *Indian J. Agr. Sci.* 40:933-934, 1970.
2. Allen, Stewart E., Alan Carlisle, Eric James White, and C. C. Evans. Plant Nutrient Content of Rainwater. *J. Ecol.* 56:497-504, 1968.
3. Andersson, Tage. Small-Scale Variations of the Contamination of Rain Caused by Washout from the Low Layers of the Atmosphere. *Tellus.* 21:685-692, 1969.
4. Bhandari, Narendra and Devendra Lal. Vertical Structure of the Troposphere as Revealed by Radioactive Tracer Studies. *J. Geophys. Res.* 75:2974-2980, 1970.
5. Boutron, C., M. Echevin, and C. Lorius. Chemistry of Polar Snow, Estimation of Rates of Deposition in Antarctica. *Geochim. Cosmochim. Acta.* 36:1029-1041, 1972.
6. Chojnacki, Adam. Chemical Composition of Atmospheric Precipitations in Poland. II. *Pamiet. Pulawski.* 29:163-170, 1967. (Pol)
7. Chojnacki, Adam. Chemical Composition of Atmospheric Precipitations in Poland. III. *Pamiet. Pulawski.* 29:171-184, 1967. (Pol)
8. Chojnacki, A. and M. Kac-Kacas. Content of Some Nutrition Components in Precipitation in Poland in the Pulawy Region. *Tellus.* 15:202-203, 1963.
9. Dansgaard, W. Stable Isotopes in Precipitation. *Tellus.* 16:436-468, 1964.
10. Derpgol'ts, V. F. The Geochemical Description of Meteoric Waters of the Enisei Sector of the Arctic Region. *Dokl. Akad. Nauk SSSR* 178: 702-705, 1968. (Russ)

11. Dingle, A. and D. Gatz. Trace Substances in Rainwater: Concentration Variations During Convective Rains and Their Interpretation. *Tellus*. 23:14-27, 1971.
12. Egner, H. and E. Erikssen. Current Data on the Chemical Composition of Air and Precipitation. *Tellus*. 7:134-139, 1955.
13. Emanuelsson, A., E. Eriksson and H. Eggner. Composition of Atmospheric Precipitation in Sweden. *Tellus*. 6:261-264, 1954.
14. Faugere, J. G. Atmospheric Pollution in the Built-up Area. *Pollut. Atmos.* 13:17-22, 1971.(Fr)
15. Feth, J. H. Chemical Characteristics of Bulk Precipitation in the Mojave Desert Region, California. U. S. Geol. Surv. Prof. Paper Number 575-C 222-7, 1967.
16. Fisher, Donald W. Annual Variations in Chemical Composition of Atmospheric Precipitation in Eastern North Carolina and Southeastern Virginia. U. S. Geol. Surv. Water-Supply Paper No. 1535-M, 1968, 21 p.
17. Fleetwood, A. The Chemical Composition of the Precipitation and Surface Water and Its Relation to Evaporation on Bjørnøya Island, Norway. *Tellus*. 21:113-126, 1969.
18. Gambell, A. W. and D. W. Fisher. Occurrence of Sulfate and Nitrate in Rainfall. *J. Geophys. Res.* 69:4203-4210, 1964.
19. Gorham, E. The Influence and Importance of Daily Weather Conditions in the Supply of Chloride Sulphate and Other Ions to Fresh Waters from Atmospheric Precipitation. *Phil. Trans. Roy. Soc. London*. 241:147-178, 1958.
20. Granat, L. On the Relation Between pH and the Chemical Composition in Atmospheric Precipitation. *Tellus*. 24:550-560, 1972.
21. Handa, B. K. Chemical Composition of Monsoon Rains Over Calcutta. *Tellus*. 21:95-106, 1969.
22. Handa, Baldev K. Chemical Composition of Premonsoon Showers Over Calcutta in 1968. *Sci. Cult.* 36:124-125, 1970.
23. Handa, Baldev K. Chemical Composition of Rainwater in Some Parts of Northern India. *Indian J. Meteorol. Geophys.* 19:175-180, 1968.
24. Herman, F. A. and E. Gorham. Total Mineral Material, Acidity, Sulfur, and Nitrogen in Rain and Snow at Kentville, Nova Scotia. *Tellus*. 9:180-183, 1957.

25. Hutton, J. T. Redistribution of the More Soluble Chemical Elements Associated with Soils as Indicated by Analysis of Rainwater, Soils, and Plants. *Trans. Int. Congress Soil Sci.* 9th. 4:313-322, 1968.
26. Junge, C. E. and P. E. Gustafson. On the Distribution of Sea-Salt Over the United States and Its Removal by Precipitation. *Tellus.* 9:164-173, 1957.
27. Junge, C. E. and R. T. Werby. The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rainwater Over the United States. *J. of Meteor.* 15:417-425, 1958.
28. Khemani, L. T. and B. V. R. Murty. Chemical Composition of Rainwater and Rain Characteristics at Delhi. *Tellus.* 20:284-292, 1968.
29. Kruger, Paul. Influence of Inversions Upon Precipitation Deposition of Radioactive Aerosols. *Tellus.* 18:516-524, 1966.
30. Lag, J. Relations Between the Chemical Composition of the Precipitation and the Contents of Exchangeable Ions in the Humus Layer of Natural Soils. *Acta Agr. Scand.* 18:148-152, 1968.
31. Larsson, T. E. and I. Hettick. Mineral Composition of Rainwater. *Tellus.* 8:191-201, 1956.
32. Lazrus, Allan L., H. W. Baynton, and James P. Lodge, Jr. Trace Constituents in Oceanic Cloud Water and Their Origin. *Tellus.* 22:106-114, 1970.
33. Low, A. J. and E. R. Armitage. Composition of the Leachate Through Cropped and Uncropped Soils in Lysimeters Compared with That of the Rain. *Plant Soil.* 33:393-411, 1970.
34. MacIntire, W. H. and J. B. Young. Sulfur, Calcium, Magnesium and Potassium Content and Reaction of Rainfall at Different Points in Tennessee. *Soil Science.* 15:205-227, 1923.
35. Martens, C. S. and R. C. Harriss. Chemistry of Aerosols, Cloud Droplets and Rain in the Puerto Rican Marine Atmosphere. *J. Geophys. Res.* 78:949-957, 1973.
36. Masiliunas, L. and G. Pauliukevicius. Topographicgeochemical Zoning and Biogeochemical Characteristics of Lithuanian Topography, IV. Chemical Composition of Autumn Atmospheric Rainfall and Washing Out of Chemical Materials from Tree Foliage. *Liet. TSR Mokslu Akad. Darb. Ser. B.* 1:229-240, 1969. (Russ)
37. Meetham, A. R. Natural Removal of Pollution From the Atmosphere. *Q. J. Roy. Met. Soc.* 76:359-371, 1950.

38. Munn, R. E. and H. Rodhe. On the Meteorological Interpretation of the Chemical Composition of Monthly Precipitation Samples. *Tellus*. 22: 137-139, 1970.
39. Munn, R. E. and H. Rodhe. On the Meteorological Interpretation of the Chemical Composition of Monthly Precipitation Samples. *Tellus*. 23:1-13, 1971.
40. Murty, A. S. and Bh. V. Murty. Source of Origin of Ice-Forming Aerosols As Suggested by Measurements on the Soluble and Nonsoluble Components of Rainwater. *Tellus*. 22:228-234, 1970.
41. Nasimov, T. N. Concise Characteristics of the Chemical Composition of Atmospheric Precipitation in the Kara-Mazar Mountains. *Dokl. Akad. Nauk. Tadzh. SSR* 13:51-52, 1970. (Russ)
42. Oddie, B. C. V. The Chemical Composition of Precipitation at Various Cloud Levels. *Q. J. Roy. Met. Soc.* 88:535-538, 1962.
43. O'Hare, P. J. The Leaching of Nutrients by Rain Water From Forest Trees. *Colloq. Forest Fert. Proc. Colloq. Int. Potash Inst.*, 5th. 1966. (Pub. 1967.)
44. Osipova, A. Chemical Composition of Atmospheric Precipitation in the Chon-Zyzyl-Su River Basin. *Vop. Vod. Khoz.*, No. 3 (Pt. 1), 4-8 (Russ) 1968. From *Ref. Zh., Khim.* Abstract No. 21225, 1968.
45. Perkins, Richard W., Charles William Thomas, and James Arthur Young. Application of Short-Lived Cosmogenic Radionuclides as Tracers of In-Cloud Scavenging Processes. *J. Geophys. Res.* 75:3076-3087, 1970.
46. Petrenchuk, O. P. and V. M. Drozdova. On the Chemical Composition of Cloud Water. *Tellus*. 18:280-286, 1966.
47. Petrenchuk, O. P. and V. M. Drozdova. The Chemical Composition of Cloud Water in Kazan and Adjacent Areas. *Tr. Gl. Geofiz. Observ.* 238:209-209, 1969. (Russ)
48. Petrenchuk, O. P., V. M. Drozdova, and M. A. Belyashova. Chemical Composition of Cloud Water in Relation to Various Cloud Microstructures. *Chem. Abstracts* 69:79317q. 1968. (Russ)
49. Posokhov, E. V. Factors Affecting the Chemical Composition of Rain. *Gidrokhim. Mater.* 46:15-31, 1968. (Russ)
50. Rodhe, H. and J. Grandell. On the Removal Time of Aerosol Particles from the Atmosphere by Precipitation Scavenging. *Tellus*. 24:442-444, 1972.

51. Rubeikin, V. Z. Formation of the Chemical Constitution of Atmospheric Precipitation. Dokl. Akad. Nauk SSSR. 191:931-934, 1970.
52. Rutherford, G. K. Preliminary Study of the Composition of Precipitation. Can. J. Earth Sci. 4:1151-1160, 1967.
53. Sardarov, E. I. and G. S. Khachatryan. Chemical Composition of Atmospheric Precipitations in the Central Volcanic Highlands of the Armenian S.S.R. Izv. Akad. Nauk Arm. SSR, Nauki Zemle 20: 101-108, 1967.
54. Selezneva, E. S. Condensation Nuclei and Chemical Composition of Atmospheric Precipitations. Tr. Gl. Geofiz. Observ. 218:241-250, 1967.
55. Selezneva, E. S. Relation Between Mineralization and Electrical Conductivity of Atmospheric Precipitation. Tr. Gl. Geofiz. Observ. 234:208-212, 1968. (Russ)
56. Selezneva, E. S. Estimation of the Background Contamination of the Atmosphere from the Chemical Composition of Precipitation. Tellus. 24:122-128, 1972.
57. Supatashvili, G. D., A. I. Kartsivadze, L. Sh. Abesalashvili, and N. K. Karsanidze. Trace Elements in the Precipitation of the Alazani Valley. Soobshch. Akad. Nauk Gruz. SSR. 66:121-124, 1972. (Russ)
58. Tkachenko, K. D. and P. I. Kolesnik. Chemical Composition of Atmospheric Precipitation Near Kiev. Meteorol. Gibrol. 13:192-197 1969. (Russ)
59. Windsor, G. J. Dynamics of Phosphorus, Silicon, Iron and Aluminum Movement in Gravitational Rainwater in a Douglas-Fir Ecosystem. University of Washington. Order No. 70-14,796, 1969.
60. Woodcock, A. H. Atmospheric Salt Particles and Raindrops. J. Met. 9:200-212, 1952.
61. Zverev, V. P. Role of Rainfall in the Circulation of Chemical Elements Between the Atmosphere and the Lithosphere. Dokl. Akad. Nauk SSSR 181:716-719, 1968. (Russ)

GENERAL

1. Carrol, D. Rainwater as a Chemical Agent of Geologic Processes--A Review. Geol. Surv. Water-Supply Paper 1535 G, 1962.

2. Engelmann, R. J. Scavenging Prediction Using Ratios of Concentrations in Air and Precipitation. *J. Appl. Meteorol.* 10:493-497, 1971.
3. Gatz, D. F. Deposition of Atmospheric Particulate Matter by Convective Storms: The Role of the Convective Updraft as an Input Mechanism and Dissertation. University of Michigan, Ann Arbor, 1966.
4. Georgii, H. W. and Erich Weber. Investigations on Tropospheric Washout. Johann Wolfgang Goethe-Universitaat, Institut für Meteorologie und Geophysik. Technical Report. August 1964.
5. Georgii, H. W. Untersuchung über das Auswaschen atmosphärischer Spurenstoffe durch den Niederschlag. Die Meteorologische Tagung in Hamburg 1962. *Berichte des Deutschen Wetterdienstes* Nr. 91:108-111.
6. Hales, J. M. Fundamentals of the Theory of Gas Scavenging by Rain. *Atmospheric Environment.* 6:635-639, 1972.
7. Junge, C. E. Air Chemistry and Radioactivity. Academic Press, New York. 1963.
8. Junge, C. E. and P. E. Gustafson. Precipitation Sampling for Chemical Analysis. *Bull. Am. Met. Soc.* 37:244, 1956.
9. Kramer, James R. Fate of Atmospheric Sulfur Dioxide and Related Substances as Indicated by Chemistry of Precipitation. Final Report to Ministry of Environment, Canada. June 1973.
10. Likens, G. E. The Chemistry of Precipitation in the Central Finger Lakes Region. Cornell Univ. Water Resources and Marine Sciences Center, Ithaca, N. Y. 1972.
11. Lodge, et al. Chemistry of United States Precipitation. Final Report on the National Precipitation Sampling Network. NCAR, Boulder, Colorado. 1968.
12. Petrenchuck, O. P. and V. M. Drozdova. On the Chemical Composition of Cloud Water. *Tellus.* 18:280-286, 1966.